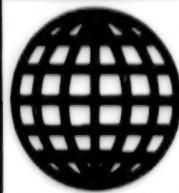


JPRS-UCH-92-007

21 October 1992



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# ***JPRS Report***

## **Science & Technology**

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***Central Eurasia:  
Chemistry***

# Science & Technology

## CENTRAL EURASIA: Chemistry

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**The Effect of an NaY Zeolite in the Aluminosilicate Matrix on the Properties of Palladium Catalysts and Their Activity in the Oxidation of CO**

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received 24 May 91) pp 56-60

[Article by V.Z. Radkevich, M.F. Savchits, P.V. Kurman, A.G. Kekalo, and Yu.G. Yegiazarov, Physical and Organic Chemistry Institute, Byelarus Academy of Sciences; UDC 66.094.373(661.183.6:546.98)]

[Abstract] The authors of the study reported herein examined the effect that water-soluble surfactants and emulsions of a second type with the same type of emulsifier have on the lyophilicity of dispersions of natural minerals in an apolar medium. As study objects, the researchers used suspensions of materials with different degrees of hydrophilicity, i.e., montmorillonite, calcite, and graphite (with respective wetting heats of 70, 1.3, and 1.0 J/g) in a diesel fuel distillate. The emulsions referred to as "emulsions of the second type" were prepared by using a variety of chemicals as emulsifiers of oil-soluble surfactants. Specifically, they used monoethanolamide (selected as a representative nonionogenic surfactant), an organomineral compound based on a product of the reaction of oleic acid, sodium silicate, and trivalent iron salt (selected as a representative anionic surfactant), and an ester of carbonic acids and triethanolamine (selected as a representative cationic surfactant). The emulsions had a concentration of 50% with respect to the hydrocarbon phase and between 2 and 5% with respect to the emulsifier. The amount of emulsifier used as a modifier was varied from 0 to 20% of the mass of the disperse phase of the suspensions. The change in hydrophilic-lyophilic properties of the mineral suspensions in an apolar medium was judged by the change in moisture absorption for both the starting and modified mineral specimens as determined by the threshold moisture and wetting heat methods. The studies performed established that the nature of the dependence of the lyophilic properties of modified minerals varies significantly for minerals whose surfaces have different starting hydrophilicities. In the case of the hydrophilic mineral montmorillonite, for example, as the amount of modifying emulsion was increased, the hydrophilicity with respect to the quantity of water vapors absorbed proved to be extremal: Minimum values were found at low concentrations, and higher values were found at higher concentrations. In the case of the hydrophobic mineral graphite, on the other hand, two maxima were evident on the curves illustrating the dependence of moisture absorption on the quantity of modifying surfactant, thus confirming the successive hydrophilization of the system at both low and high modifier concentrations. Minerals with low hydrophilicity (specifically, calcite) were found to occupy an intermediate position, which is to say that the change in the hydrophilicity of their surface at low

modifier concentrations was the same as that for hydrophobic materials, whereas ... was the same as that for hydrophilic materials at higher concentrations of modifying surfactant. Further studies revealed that the effects of hydrophobization and hydrophilization intensify as the particle size of the starting mineral is increased. Individual surfactants were found to be the most effective hydrophobizing agents. Figures 3, table 1; references 15: 9 Russian, 6 Western.

**Secondary Combustion of Hydrogen by Oxygen on a  $\text{Co}_3\text{O}_4/\text{SiO}_2$  Catalyst**

927M0120B Minsk AKADEMII NAUK  
BELORUSSKOY SSR: SERIYA KHIMICHESKIH  
NAUK in Russian No 2, Mar-Apr 92 (manuscript  
received 17 Jul 91) pp 114-115

[Article by G.I. Novikov, T.N. Dovbysheva, V.V. Demyanchuk, and P.O. Gorbonos; UDC 541.128.13]

[Abstract] The authors of the study reported herein worked to find an effective non-precious metal-containing catalyst that could be used to burn oxyhydrogen in the presence of saturated steam. Specifically, they examined the feasibility of using a  $\text{Co}_3\text{O}_4$  catalyst on a silica fiber with a very developed surface and developed a method of applying the said catalyst onto fiber that would result in a catalyst-carrier contact with sufficient mechanical strength. The catalyst was produced by impregnating degreased silica fiber in a cobalt nitrate solution for several days and then treating it with bromine in an alkaline medium. The precipitated hydrate of cobalt oxide was rinsed by the decantation method, filtered, dried, and then held in a vacuum for 8 to 9 hours at a temperature of 273 to 288 K. During that time the cobalt oxide hydrate was transformed into  $\text{Co}_3\text{O}_4$ . The surface of the silica fiber, as determined by the method of thermal desorption of argon, amounted to  $15.6 \text{ m}^2/\text{g}$ . The method of gas-phase heterogeneous catalytic oxidation of hydrogen by oxygen in a continuous reactor was used as the basis for the experiments conducted. Before being added to the reactor, the gas mixture was saturated with steam at a temperature of 353 K, which resulted in a pressure of 48.1 kPa. The space velocity of the gas mixture was varied from 8.40 to 23.3 l/h. The change in the composition of the gas mixture during the course of the reaction at temperatures of 473, 498, and 523 K and at a saturated-steam pressure of 48.53 kPa were recorded and presented in table form. When the temperature of the catalyst was changed from 473 to 523 K, the effective reaction rate constant increased from 0.3 to  $6.2 \text{ s}^{-1}$ . Figure 1, table 1; references 2 (Russian).

**Activity of Cracking Catalysts Containing Zeolites With Different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  Ratios**

927M0130A St. Petersburg ZHURNAL PRIKLADNOY  
KHIMII in Russian Vol 64 No 12, Dec 91 (manuscript  
received 4 Mar 91) pp 2542-2547

[Article by L.P. Maksimyuk, I.M. Kolesnikov, and D.S. Okonkvo, Moscow Oil and Gas Institute imeni I.M. Gubkin; UDC 541.128]

**[Abstract]** The authors of the study reported herein examined the activity and selectivity of cracking catalysts containing zeolites with different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios. Gas oil was subjected to vacuum cracking in a continuous reactor to which 18 g of microspheric-type catalyst had been added. Before the experiment, the fresh catalyst was stabilized in a stream of steam for 6 hours at a temperature of 998 K. The catalyst was layered into the reactor together with crushed quartz. The vacuum cracking was conducted at a temperature of 773 K while the raw material was fed in at a rate of 20 g/(g x h) for 2.5 minutes. The catalyst was collected into a glass receptacle and fractioned. The  $C_5$  benzene (473 K) and light gas oil (473 to 523 K) fractions were withdrawn. Chromatography studies were performed on the gaseous cracking products in a mix with nitrogen that had been blown into the reaction system for 10 minutes at a rate of 18 l/h after the process had been completed. Three catalysts produced by the firm Grace, i.e., DA-300, Nova-D, and Rezok-1, were used. Each had a different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, with Rezok-1 having the highest and DA-300 having the lowest ratio. The conversion of the gas oil was determined as the sum of the yields of the gaseous products benzene and coke. The studies performed established that cracking catalyst activity increases as the catalyst's  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio increases. The catalysts studied were found to have the following dynamic activities: DA-300, 0.39; Nova-D, 0.48; and Rezok-1, 0.52. Rezok-1 was found to have the highest selectivity with respect to olefin yield and the lowest selectivity with respect to coke yield. Nova-D was found to have the highest selectivity with respect to benzene yield and moderate coke formation. Figures 1, tables 2; references 11: 8 Russian, 3 Western.

### Hydrogenation Catalysts Based on Complexes of Palladium (II) With Polyvinylpyridines

927M0130B St. Petersburg ZHURNAL PRIKLADNOY KHIMII in Russian Vol 64 No 12, Dec 91 (manuscript received 17 Apr 91) pp 2547-2551

[Article by A.K. Zharmagambetova, S.G. Mukhamedzhanova, Ye.A. Bekturov, and Yu.P. Saltykov, Organic Catalysis and Electrochemistry Institute imeni D.V. Sokolskiy; UDC 541.128:67.744]

**[Abstract]** The authors of the study reported herein examined the effect that the conditions of producing complexes of palladium (II) with poly-2-vinylpyridine have on their catalytic activity in the hydrogenation of 2-propen-1-ol. The hydrogenation was conducted in water at the atmospheric pressure of hydrogen and a temperature of 25°. The complexes (weight, 0.3 g) were placed into a reactor with water (25 ml) and saturated with hydrogen for 30 minutes, after which time 2-propen-1-ol (0.18 mol/l) was added. In some of the experiments the polymer-metal complexes were pretreated with sodium borohydride in water, rinsed, and then placed in the reactor. The initial method used to prepare the complexes was based on reacting ethanol

solutions of  $\text{PdCl}_2$  stabilized with HCl and poly-2-vinylpyridine. Portions of catalyst were extracted from the mother liquor 2 hours, 7 hours, and 1, 3, 7, 10, and 30 days after its formation. All of the extracted portions of catalyst were rinsed in ethanol and air-dried. Catalysts with polyvinylpyridine-to-palladium ratios of 1:1, 2:1, 5:1, 10:1, and 25:1 were studied. The catalyst with the 1:1 polyvinylpyridine-to-palladium ratio resulted in the most rapid hydrogenation. Doubling the amount of polymer when the polymer-metal complex was prepared was found to result in a complex that was approximately half as active as the catalyst with the 1:1 ratio. Further increasing the polymer-to-metal ratio did not appear to affect the activity of the resultant complexes. All of the five catalysts tested proved to be highly stable in the hydrogenation of successive portions of 2-propen-1-ol. Specimens of the catalyst with a 1:1 polymer-to-metal ratio were heated to 25, 30, 50, 60, and 80°. The maximum hydrogenation rate was achieved in the case of the specimen prepared at 50°. The specimens prepared at 25 and 30° proved to have low activity levels, as did the specimen heated to 80°. Increasing the temperature of the starting solutions to 50-60° thus proved to be best. Pretreating the catalysts with sodium borohydride was found to increase catalyst activity by a factor of 5 to 5.5. Figures 4, table 1; references 13: 8 Russian, 5 Western.

### The Parameters of a Layer of Semiconductor Epitaxial III-V Heterostructures as a Function of Liquid-Phase Epitaxy Conditions (by Way of the Example of In-Ga-As-Sb)

927M0130C St. Petersburg ZHURNAL PRIKLADNOY KHIMII in Russian Vol 64 No 12, Dec 91 (manuscript received 2 Nov 90) pp 2587-2592

[Article by A.M. Grebenyuk, A.M. Litvak, A.A. Popov, S.V. Syavris, and N.A. Charykov, Physics and Technology Institute imeni A.F. Ioffe, Russian Academy of Sciences; UDC 621.315.592]

**[Abstract]** The authors of the study reported herein have examined the effect that the conditions under which liquid-phase epitaxy is performed have on the growth of semiconductor epitaxial III-V heterostructures. Specifically, they have examined the effects of the initially crystallized liquid- and solid-phase compositions and the temperature of the initiation of epitaxial growth. The system In-Ga-As-Sb was studied as an example system; however, the results may be extended to other III-V systems without any qualitative changes. In the examples considered, the melt weighed 1 g, the surface area measured 1 cm<sup>2</sup>, and the temperature of the initiation of crystallization was 600°. The melt was assumed to be molecular. The analysis performed indicated that at the epitaxy temperature considered, the growth parameters of the epilayers worsen as the limiting compositions are approached: The result is thinner epilayers with a greater lattice period mismatch and with a greater variation in the width of the forbidden band along the direction that is oriented normal to the substrate. The epilayers' growth parameters were also shown to worsen when the epitaxy

temperature is reduced in cases where the composition of the synthesized solid solution has been held steady. The studies further demonstrated that the highest-quality III-V epilayers are obtained when the maximum possible epitaxy temperature is used (i.e., the temperature corresponding to what is termed a molecular melt). For the solid solution InGaAsSb/GaSb (compositions close to GaSb), 570° is the minimum temperature that should be used. For compositions close to InAs, the minimum temperature is 564°, and for InAsSbP/InAs, the minimum temperature is 541°. They caution that the algorithm they used to plot the crystallization curves presented is designed for use in cases of quasi-liquid phase epitaxy, which is to say that it is based on the assumptions that the crystal system cools rather slowly and that diffusion is instantaneous. If the cooling rate is faster, that part of the melt that is adjacent to the substrate will change its composition faster than the entire mass of the melt will. Studies of the dependence of the thicknesses and compositions of epilayers at cooling rates of 0.15, 0.30, and 0.50 °/min demonstrated that the results of liquid-phase epitaxy are independent of the cooling rate. Calculations further indicated that when a mismatch of lattice periods of  $\Delta a \approx 0.005$  to 0.020 accumulates, crystallization on the substrate ceases. This is because crystallization in the bulk of the melt becomes more advantageous. Figures 3; references 14: 11 Russian, 3 Western.

### Flow Resistance of Catalysts With Different Grain Shapes

927M0130E St. Petersburg ZHURNAL PRIKLADNOY KHIMII in Russian Vol 64 No 12, Dec 91 (manuscript received 12 Jul 91) pp 2661-2665

[Article by V.I. Malkiman, I.A. Kravtsova, L.M. Gribanova, L.N. Kazennykh, Ural Chemistry Scientific Research Institute; UDC 541.128]

[Abstract] The authors of the study reported herein worked to determine those hydraulic characteristics of a layer of SVS industrial vanadium catalyst with grains of different shapes that are needed to calculate flow resistance. Specifically, they calculated the following characteristics:  $\varepsilon$  (the percentage of the layer that represents free volume, which is to say the layer's porosity);  $S_0$  (the specific surface of the grains in  $m^2/m^3$ );  $K$  (the viscosity constant of the flow resistance or drag coefficient); and  $K_i$  (the iteration constant of the drag coefficient). The apparent density was determined by the pycnometer method. A layer of catalyst 500 mm high was placed in a column measuring 150 mm in diameter. The linear flow speed of the gas was varied from 0.2 to 1.0 nm/s with an interval of 0.2 nm/s. The flow resistance was determined from three measurements. The values obtained for the viscosity and iteration drag coefficients for SVS rings and the calculated dependence of the drag coefficient on gas flow speed corresponded approximately to the data presented in the sulfuric acid specialist's manual for the rings of the vanadium catalyst BAV. Spherical granules ( $d_{av} = 7.5$  mm) were found to have the lowest flow

resistance. It was half the flow resistance calculated for an annular catalyst. The drag coefficient of rings of the catalyst SVS were calculated as  $K = 13$  to 15 and  $K_i \approx 1$ . For the catalyst BAV, values of  $K = 10$  to 11 and  $K_i = 0.9$  to 1.0 were calculated. Layers of rings with blind holes were found to have twice as high a drag coefficient as layers with through holes do. The drag coefficient of silica gel granules was found to be three- to fourfold higher than that of rings with through holes. Figures 2, tables 2; references 4 (Russian).

### Oxidation of Hydrogen by Oxygen on a Stainless Steel Catalyst

927M0131A Minsk IZVESTIYA AKADEMII NAUK BELORUSSKOY SSR: SERIYA KHMICHESKIH NAUK in Russian No 1, Jan 92 (manuscript received 10 Jul 91) pp 5-8

[Article by G.I. Novikov, T.N. Dovbyshcheva, V.V. Demyanchuk, and P.O. Gorbonos, Byelorussian Technology Institute imeni S.M. Kirov; UDC 541.128.13]

[Abstract] The authors of the study reported herein examined the process of the oxidation of hydrogen by oxygen at a low (up to 1 atm) partial water vapor pressure on a stainless steel catalyst. The technique of gas-phase heterogeneous catalytic oxidation in a continuous reactor was used. The reactor was made of Pyrex glass and had an l/d ratio of >20. The gas at the reactor entrance was saturated with water vapors with a relative moisture of close to 100%. The partial pressure of the water vapors at the specified temperature amounted to 27.08 kPa, and the total pressure in the reactor was close to atmospheric. After the catalyst had been passed through the column, samples of gas were withdrawn and subjected to chromatographic analysis at a column temperature of 293 K and with an argon carrier gas flow speed of  $0.25 \times 10^{-6} m^3/s$ . The stainless steel grid used as a catalyst was made of 03Cr18Ni9Ti steel with an inner surface of  $2.154 \text{ cm}^2$  per square centimeter of geometric area and with a porosity of 33%. Before the experiment, the stainless steel grid was conditioned with a nitrogen-hydrogen-oxygen mixture for 2 hours at the experiment temperatures. The composition of the gas mixture during the course of the reaction was measured at temperatures of 683, 713, and 743 K. The effective heterogeneous reaction rate constants calculated at the said temperatures amounted to 1, 1.4, and  $2.31 \text{ s}^{-1}$ , respectively. Figures 2, table 1; references 2 (Russian).

### Oxidation of Hydrogen by Oxygen on a $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$ Catalyst in the Presence of Water Vapors

927M0131B Minsk IZVESTIYA AKADEMII NAUK BELORUSSKOY SSR: SERIYA KHMICHESKIH NAUK in Russian No 1, Jan 92 (manuscript received 10 Jul 91) pp 9-12

[Article by G.I. Novikov, T.N. Dovbyshcheva, V.V. Demyanchuk, and P.O. Gorbonos, Byelorussian Technology Institute imeni S.M. Kirov; UDC 541.128.13]

[Abstract] Others have shown that the catalyst cobalt cobaltite has a catalytic activity of 50% in the absence of water vapors. In the presence of a water vapor pressure of 2.73 kPa, on the other hand, cobalt cobaltite's activity as measured by its degree of hydrogen transformation drops to 7%. The authors of the study reported herein conducted their own examination of the oxidation of hydrogen by oxygen on a  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  catalyst in the presence of water vapors. They demonstrated that by changing the conditions and method of synthesizing cobalt cobaltite catalyst and by reducing the process temperature from the 463-493 K reported elsewhere to 423 K, it is possible to sharply increase cobalt cobaltite's catalytic activity, even in the presence of water vapors. The new method developed by the authors entails applying cobalt cobaltite to an aluminum oxide carrier. The catalyst is applied to the carrier by impregnating degreased (by alcohol) aluminum oxide fibers with a cobalt (II) nitrate solution for a day at a temperature of 333 K and then treating it with bromine in an alkaline medium. After filtration the fibers are held at a temperature of 423-453 K and a pressure of  $1.33 \times 10^{-3}$  kPa. Cobalt cobaltite forms on the aluminum oxide fiber during this holding period. The surface of the aluminum oxide fiber has a surface of  $28.2 \text{ m}^2/\text{g}$ , and the catalyst-to-carrier ratio equals 1.14 g/g. The kinetics of the process of oxidation of hydrogen by oxygen on a  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$  catalyst produced by the recommended technique were conducted in a continuous reactor. The studies performed indicated that as the catalyst temperature is increased (while the water vapor pressure is kept constant), the effective rate constant increases from 1.45 to  $9.3 \text{ s}^{-1}$ . The degree of transformation of hydrogen into water was found to decrease as the pressure of the hydrogen vapors is increased from 2.73 to 48.93 kPa. Figure 1, tables 3; references 10 (Russian).

#### **Effect of the Conditions of the Modification of H-TsVM Zeolite on Its Catalytic Properties in the Aklylation of Toluene by Ethylene**

927M0131C Minsk IZVESTIYA AKADEMII NAUK BELORUSSKOY SSR: SERIYA KHIMICHESKIH NAUK in Russian No 1, Jan 92 (manuscript received 5 Aug 91) pp 17-22

[Article by Ye.A. Stepanova, V.S. Komarov, and L.P. Shirinskaya, General and Inorganic Chemistry Institute, Belarus Academy of Sciences; UDC 541.128+547.532+542.952.537]

[Abstract] The authors of the study reported herein examined the effects that the techniques and conditions of modifying H-TsVM zeolite have on its catalytic activity in the oxidation of toluene by ethylene. The catalysts studied were produced on the basis of NaTsVM with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratios of 31.9 and 42.3 by transforming it into its  $\text{NH}_4$  form followed by roasting at 550°C as described elsewhere.  $\text{Mg}^{2+}$  cations were added to the specimens by impregnating the zeolite with a magnesium salt solution or by ion exchange. The catalytic properties of the modified zeolites were studied at

atmospheric pressure, at a temperature of 360 to 420°C, and with a molar ratio of toluene to ethylene ranging from 0.5:1 to 2:1. Gas-liquid chromatography was used to analyze the reaction products, and infrared spectroscopy based on pyridine adsorption in a high-vacuum unit as described elsewhere was used to determine their acid properties. Sixteen different combinations of catalyst compositions and synthesis regimens were examined. The experiments revealed that the nature of the salt has a strong effect on catalytic activity; for example,  $\text{MgCl}_2$  results in much lower target product yields than  $\text{MgSO}_4$  does. Catalysts containing phosphorus in addition to magnesium were found to be more selective. The order in which magnesium and phosphorus are added was also found to affect catalytic activity. Adding the phosphorus first greatly reduced catalytic activity. The conditions and technique used to add the phosphorus were also important. The studies further indicated that the role of the steric factor under zeolite impregnation conditions must also be taken into consideration in cases of powder and table zeolites. The compositions, modification conditions, activity, and selectivity of the 16 catalysts studied are summarized in two detailed tables. The studies performed thus confirmed that strict adherence to specified zeolite impregnation and heat treatment regimens is necessary if active and selective oxidation catalysts are to be produced and that deviations from the optimal regimens will result in a sharp increase in side reactions that will in turn reduce the activity and selectivity of the alkylation process. Figure 1, tables 3; references 10: 8 Russian, 2 Western.

#### **The Mechanism of Catalysts' Effect in the Alkaline Cooking of Vegetable Matter**

927M0131D Minsk IZVESTIYA AKADEMII NAUK BELORUSSKOY SSR: SERIYA KHIMICHESKIH NAUK in Russian No 1, Jan 92 (manuscript received 24 Jun 91) pp 62-66

[Article by I.I. Karpunin and M.P. Muzychenko, ByelNIIlna [not further identified] and Belarus Technology Institute imeni S.M. Kirov; UDC 676.1.022]

[Abstract] In previous publications, the authors of the study reported herein established the benefits that adding selecting metal salts of variable valence (catalysts) has on the process of the alkaline cooking of vegetable matter. In this communication they turn their attention to the mechanism of the effect of the said catalysts. Specifically, they hypothesize that in the presence of a catalyst, the ions of the reducing agent used in the process of alkaline cooking of vegetable matter may attack and reduce the hydroxyl ions or polymer radicals (including the lignin double bonds). This in turn slows the condensation-polymerization reactions of the lignin hydrolysis products that are split off. For their studies, the researchers used grist-free pine filings measuring 1 to 2 mm and  $\beta$ -coniferyl ether of guaiacyl glycerin and dehydrodiisoeugenol. To the cooking liquor they added 10% hydrazine-hydrate and 0.05% acetic acid salts of nickel and copper to a weighted portion of the material

used for cooking. A cooking temperature of 170°C was used. The processes occurring with and without the addition of the metal salts (catalysts) were compared. The comparison confirmed that adding the acetic acid salts of nickel and copper accelerated the delignification of the vegetable matter. The addition of organic matter (hydrazine-hydrin) also proved to accelerate delignification. The greatest increase in the delignification rate was obtained when a combination of the catalyst and organic matter was added to the cooking liquor. The fact that the delignification rate increased while the polymer formation rate decreased was taken as a confirmation of the catalytic effect of adding a diluted salt of metals of variable valence. Figure 1, table 1; references 20: 12 Russian, 8 Western.

#### **Electrochemical Reducing Amination. Part 1. Amination of Aliphatic Ketones with Primary Amines**

927M0152A St. Petersburg ZHURNAL  
ORGANICHESKOY KHIMII in Russian  
Vol 28, No 1, Jan 92 (manuscript received  
25 Jan 90) pp 51-58

[Article by Yu. D. Smirnov and A. P. Tomilov;  
UDC 547.284+547.233.1:541.13]

[Abstract] Reducing amination is one of the most available methods for synthesizing secondary amines. It consists primarily of the catalytic hydrogenation of a mixture of carbonyl compounds and either ammonia or a primary amine. However, this reaction requires temperatures up to 150°C and pressures to 150 atm. and therefore requires special equipment under laboratory conditions. In order to make this method more available for laboratory conditions, attempts have been made to use other reducing agents or electrochemical means. In the present work aliphatic ketones were electrochemically reduced in aqueous solutions of primary amines. Optimum yields were obtained with lead and cadmium cathodes at pH 11-12. Elongation and branching of the carbon chain in both the ketone and the primary amine radical causes a decrease in the yield of secondary amine. The yield of secondary amine is largely determined by the reaction rate of formation of the azomethine compound which precedes the electrochemical reduction stage. Figures 2; references 10: 3 Russian, 7 Western.

#### **Reaction of 1-Hydroxyadamanthane with Aromatic Amines in Presence of Ortho-Alkylating Catalysts**

927M0152B St. Petersburg ZHURNAL  
ORGANICHESKOY KHIMII in Russian  
Vol 28, No 1, Jan 92 (manuscript received  
15 Mar 90) pp 182-187

[Article by D. I. Olifirov, V. A. Koshchiy, and Ya. B. Kozlikovskiy, Kiev Polytechnical Institute; UDC 547.551.1]

[Abstract] It has been demonstrated previously that aluminum anilide is an effective catalyst for ortho-alkylation of aniline with olefins. This catalyst was also used in the alkylation of aniline with 1-hydroxyadamanthane. To circumvent the negative effects of water of reaction reacting with the aluminum anilide, a special solvent was used which forms an azeotropic mixture with liberated water. The literature also contains references to the possibility of using hydrochlorides of corresponding amines as catalysts in the ortho-alkylation of aromatic amines with olefins. Therefore, in the present work a mixture of mono- and di(1-adamantyl)-anilines and 4,4'-di(1-adamantyl)diphenylamine was used as catalyst in the reaction of 1-hydroxyadamanthane with aniline and N-methylamine. Higher yields were obtained with aluminum anilide as catalyst. References 7: 4 Russian, 3 Western.

#### **Acid Catalyzed Reaction of 1-Adamantanole with 2-Chloro- and 2,3-Dichloro-1-propenes**

927M0152C St. Petersburg ZHURNAL  
ORGANICHESKOY KHIMII in Russian  
Vol 28, No 1, Jan 92 (manuscript received  
21 May 91) pp 207-208

[Article by Yu. N. Klimochkin and I. K. Moiseyev,  
Samarsk Polytechnical Institute; UDC 547.495.3]

[Abstract] The synthesis of 1-adamanthylacetic and 1-adamanthylchloracetic acids by reaction of halogen derivatives of adamanthane with 1,1-dichloroethene and trichloroethene in acid media is well known. In the present work it was demonstrated that 1-adamanthane or its nitrate reacts with 2-chloro-1-propene in the presence of concentrated sulfuric acid to form a mixture of 1-chloroadamanthane and 1-adamanthylacetone. The ketone is evidently formed by reaction with an intermediate. References 4: 2 Russian, 2 Western.

#### **Characteristics of Process Mechanisms Accompanied by Change in Catalyst Activity**

927M0162A Moscow KINETIKA I KATALIZ  
in Russian Vol 33 No 3 May-Jun 92 (manuscript  
received 24 Dec 90) pp 503-515

[Article by L. Petrov, K. Kumbiliyeva, Institute of  
Kinetics and Catalysis, Bulgarian Academy of Sciences,  
Sofia; UDC 541.128.3:541.127:542.941'941.8]

[Abstract] Changes in catalytic activity play an important role, mostly a negative one, in various catalytic processes. These changes may be due to catalyst caking, poisoning by various admixtures and by the effect of the reaction mixture on the catalyst surface, even initiation of new side reactions. The last problem is the topic of this review type article covering the authors' own work and literature data. These interactions can be classified in four groups: 1) irreversible adsorption of the reactants on some active centers, removing them effectively from

catalysis; 2) reaction with a specific surface segment which may result in creation of new chemical compounds, altering the valence of the surface atoms; 3) penetration into the deeper layers of the catalyst and 4) caking with gradual deactivation of the catalyst. Since the first two types do not relate to the reaction mechanisms, only the latter two were addressed in this review. The effect of deactivation on the kinetics of catalytic processes was discussed. Cake formation has a profound effect on the reaction mechanisms; this can be modified somewhat by addition of reagents which decrease the binding strength between such caking agents and the surface of the catalyst. The article presented possible mechanisms of the cake formation and discussed various courses of the deactivation of catalysts: mass transfer of the reagents, parallel deactivation and consecutive deactivation. Figures 4; references 44: 20 Russian (1 by Western authors), 24 Western (2 by Russian authors).

### Hetero-poly-complex Catalysis of Cyclohexene Oxidation and Breakdown of Hydrogen Peroxide

927M0162B Moscow KINETIKA I KATALIZ  
in Russian Vol 33 No 3 May- Jun 92 (manuscript received 18 Mar 91) pp 516-123

[Article by N. I. Kuznetsova, L. G. Detusheva, L. I. Kuznetsova, M. A. Fedotov, V. A. Likhobolov, Institute of Catalysis, Siberian Department, Russian Academy of Sciences, Novosibirsk; UDC 541.128:541.124-145.4:542.943.7:547.592 2:549.66]

[Abstract] The effect of hetero-poly-compounds  $PW_{11}O_{39}^-$  and  $PW_{11}M(H_2O)O_{39}^{n-}$  where  $M= Ti(IV)$ ,  $V(V)$ ,  $Cr(III)$ ,  $Mn(II)$ ,  $Fe(III)$ ,  $Ni(II)$ ,  $Cu(II)$ ,  $Ru(IV)$  and  $CO(II)$  on oxidation of cyclohexene with  $H_2O_2$  was studied in acetonitrile solution. Specifically, three reactions were investigated: breakdown of hydrogen peroxide in presence of these hetero-poly-compounds, formation of the intermediate  $PW_{11}$  and  $PW_{11}M$  with  $H_2O_2$  and oxidation of cyclohexene with  $H_2O_2$  in presence of  $PW_{11}$  and  $PW_{11}M$ . The NMR  $^{31}P$  method was used to characterize these hetero-poly-anions in acetonitrile solution. The catalytic properties of these complexes differed from the starting anion  $PW_{11}O_{39}^-$  and depended on the metal ion introduced. The oxidation of cyclohexene and decomposition of hydrogen peroxide went through a formation of peroxide complexes which eventually decomposed with liberation of molecular oxygen, or were used up in oxidation of cyclohexene. Table 2; figures 3; references 18: 3 Russian, 15 Western (1 by Russian authors).

### Effect of Basicity on Oxidation of Alkanes With Sodium Hypochlorite During Catalysis With Fe(III) Tetramesityl Porphyrin: Reaction Acceleration and Selectivity Change

927M0162C Moscow KINETIKA I KATALIZ  
in Russian Vol 33 No 3 May- Jun 92 (manuscript received 2 Jul 91) pp 524-530

[Article by A. B. Sorokin, A. M. Khenkin, A. Ye. Shilov, Institute of Chemical Physics, Russian Academy of

Sciences, Chernogolovka; UDC 541.128.12:541.124-145.2:542.243.7:547.21:546.33'133.1:547.979]

[Abstract] Oxidation of hydrocarbons represents an important area of current chemical investigations. Recently the authors showed that the system of iron-porphyrin (PFeCl)-sodium hypochlorite (NaOCl) oxidized effectively and selectively alkanes to alcohols. An attempt was made to test the nucleophilic action of  $OH^-$  on the formation of an active component in this reaction. It was shown that introduction of considerable quantity of a base into the reaction mixture increased the rate and selectivity of oxidation of alkanes by the PFeCl-NaOCl system. The actual rate increased 10-fold with higher concentration of the base. Evidently, the base is coordinated into [PFe $^+$ OCl] and assist in splitting the O-Cl bond, forming a more active particle  $P^+Fe^{IV}-O$ . Another possible explanation postulated participation of the base in a transition state of the C-H bond, facilitating the breaking of the C-H bond and transferring the electron to Fe with formation of an alkoxy complex of iron-porphyrin. This then reacts with water or hypochlorite to form alcohol or a ketone, respectively. Figures 2; references 14: 4 Russian, 10 Western (3 by Russian authors).

### Ammonium Salt Catalysis of Aminolysis Reactions of Cyclic Imides of 1,2-Dicarboxylic Acids

927M0162D Moscow KINETIKA I KATALIZ  
in Russian Vol 33 No 3 May- Jun 92 (manuscript received 5 Jul 91) pp 531-534

[Article by L. D. Karat, V. I. Streletsov, Ukrainian Scientific Research Institute of Plastics, Donetsk; UDC 541.128.3:541.124-145.4:[547.584'298.2+547.822.3]:546.39]

[Abstract] One of the usual methods of the synthesis of substituted 1,2-dicarboxylic acid diamides is the aminolysis of cyclic 1,2-dicarboxylic acid imides. Literature data on the kinetics of such reactions are limited. Therefore, the kinetics of N-phenylphthalimide reaction with piperidine was studied in chlorobenzene solution using catalytic amounts of carboxylic acids and tetraalkylammonium halides. The activity of this catalyst was related to the nature of the ammonium salt cation and anion and to the structure of carboxylic acid. The reactions appeared to be of the first order in respect to the amine and imide; the rate of aminolysis was linearly related to the concentration of the catalyst. The reaction followed the mechanism of general basic catalysis. Table 1; figure 1; references 10: 9 Russian (4 by Western authors), 1 Western.

### Heterogeneous-Homogeneous Reaction Routes of Ethanol Over Sn- Mo Oxide Catalyst

927M0162E Moscow KINETIKA I KATALIZ  
in Russian Vol 33 No 3 May- Jun 92 (manuscript received 21 Dec 90) pp 571-572

[Article by V. L. Bagiyev, G. A. Dadashev, K. Yu. Adzhamov, T. G. Alkhazov, Azerbaydzhan Institute of

Petroleum and Chemistry imeni M. Azizbekov, Baku; UDC 541.128.13:541.124:542.943.7:547.261:546.811'77-31]

[Abstract] Catalytic oxidation of ethanol is one of the more promising reactions for production of acetic acid, but there are indications that this is a complex reaction with possible coexistence of heterogeneous-homogeneous stages. To shed light on this problem, oxidation of ethanol over Sn-Mo catalyst was carried out in narrow glass tubing at atmospheric pressure. In the first series of experiments, the amount of catalyst was varied from 0.5 to 1.5 g using identical cross-section tubes (10 mm); in another series 1 g of the catalyst was used while the tube diameter was varied from 6 to 16 mm. The reaction mixture consisted of ethanol:air:water vapor taken at 1:9:10 ratio. In absence of the catalyst there was no reaction observed even at 360°C. With the catalyst the oxidation occurred already at 150°C yielding acetaldehyde and acetic acid. Even small quantities of the catalyst gave greatly increased yields of acetaldehyde; further increase in the quantity of the catalyst had no additional effect. An increase in the tube diameter had no effect on CO<sub>2</sub> or on acetic acid production if the amount of catalyst was kept the same. Some of the acetic acid must have formed by oxidation of acetaldehyde and possibly some other intermediate product. The yield of acetaldehyde was linearly related to the tube diameter. Overall, the acetaldehyde formed by a heterogeneous-homogeneous route while the acetic acid and CO<sub>2</sub> formed on the surface of the catalyst. Figures 2; references: 7 (Russian).

#### Photocatalytic Oxidation of Hydrogen Over Alkali Earth Metal Fluorides

927M0162F Moscow KINETIKA I KATALIZ  
in Russian Vol 33 No 3 May-Jun 92 (manuscript received 16 Apr 91) pp 581-585

[Article by Ye. P. Meshcheryakov, A. V. Yemelin, V. K. Ryabchuk, T. S. Minakova, Tomsk State University, Scientific Research Institute of Physics, St. Petersburg State University; 541.145:542.243.7:541.124:546.11:546.442'161]

[Abstract] Earlier studies showed that photo-adsorption of both the acceptor and donor gasses occurred on Ba, Sr, Ca, Mg, K, and Cs fluorides. Due to the fact that alkali metal fluorides are effective catalysts for the photo-oxidation of H<sub>2</sub>, an assumption was made that this process could also occur on BaF<sub>2</sub>, SrF<sub>2</sub>, CaF<sub>2</sub> and MgF<sub>2</sub>. Indeed, such photo-oxidation was observed. Illumination of the system: alkali metal fluorides-photo-adsorbed O<sub>2</sub>-H<sub>2</sub> with a mercury lamp PRK-4 resulted in total disappearance of O<sub>2</sub>, provided that the quantity of H<sub>2</sub> was sufficient. Illumination of alkali metal fluorides in a mixture of hydrogen and oxygen in gaseous phase resulted in photo-oxidation of H<sub>2</sub>. This reaction reached a maximum at the moment of the disappearance of O<sub>2</sub>. Based on the kinetic data obtained, a reaction mechanism was proposed, the constants of elementary stages

were estimated and a hypothesis was postulated of the participation of electronically excited stages of the adsorbed O<sub>2</sub> in this reaction. Figures 4; references: 6 (Russian).

#### Some Kinetic Characteristics of C<sub>1</sub>-C<sub>3</sub> Alkane Conversions With Carbon Dioxide Over Manganese Containing Catalysts

927M0162G Moscow KINETIKA I KATALIZ  
in Russian Vol 33 No 3 May-Jun 92 (manuscript received 14 Jun 91) pp 591-596

[Article by S. R. Mirzabekova, A. Kh. Mamedov, V. S. Aliyev, O. V. Krylov, Institute of Petrochemical Processes imeni Yu. G. Mamedaliyev, Azerbaijan Academy of Sciences, Baku; Institute of Chemical Physics imeni N. N. Semenov, Russian Academy of Sciences, Moscow; UDC 541.128.3:541.127:[547.21+546.264-31]:546.714-44]

[Abstract] In earlier studies it was shown that conversion of methane with CO<sub>2</sub> occurs by a different mechanism than conversion of ethane and propane. It was shown that in these reactions the catalyst surface is reduced by CO formed during the reaction. In present work this reduction of the catalyst was investigated as it affected the conversion processes of C<sub>1</sub>-C<sub>3</sub> alkanes in presence of CO<sub>2</sub> used as the oxidizer. The reaction was performed at 700-850°C over a catalyst K-Cr-MnO/SiO<sub>2</sub>. It was shown that formation of CO during conversion of these alkanes has a real effect on the course of these processes and on the selectivity of the formation of ethylene. The change in the selectivity of these processes differentiates them significantly from the conversions of C<sub>1</sub>-C<sub>3</sub> alkanes in presence of oxygen. Table 1; figures 3; references 7: 5 Russian, 2 Western (1 by Russian authors).

#### Effect of Component Ratio of Catalytic System Titanium Tetrachloride-Acetophenone-Triisobutyl Aluminum on Alternating Copolymerization of Butadiene and Propylene, Based on ESR Data

927M0162H Moscow KINETIKA I KATALIZ  
in Russian Vol 33 No 3 May-Jun 92 (manuscript received 15 Oct 90) pp 597-604

[Article by L. V. Smirnova, L. A. Yatsenko, A. G. Boldyrev, V. F. Anufriyenko, E. S. Gankina, I. I. Malakhova, Ye. N. Kropacheva, Scientific Research Institute of Synthetic Rubber imeni S. V. Lebedev, St. Petersburg; UDC 541.128.3:542.952.6:547.313.3'315:[547.256.2+546.824'131-386]

[Abstract] In a previous study of alternating copolymerization of butadiene and propylene an ESR signal g=1.974 was identified, which indicated formation of a diad type copolymer -(C<sub>4</sub>H<sub>8</sub>-C<sub>3</sub>H<sub>6</sub>)-. In the present work the effect of the component ratio and of the reaction conditions on the intensity of this signal was investigated analyzing the relationship between the ESR

spectra and the activity and selectivity of the system. Analysis of the data showed that the content of diads in the copolymer and the cis- and trans-links in the butadiene portion of the chain does not depend on the initial ratio of triisobutyl aluminum and titanium tetrachloride at  $2.5 \leq Al/Ti \leq 6$ . Excess of aluminum organic compound lowers the stability of the active complex and the yield of the polymer. In case of a lower ratio of Al/Ti (2.2), in spite of the increased stability of the complex  $Ti^{3+}$  compounds, the activity of the system is lower. An assumption was expressed that pre-reaction complexes with  $g = 1.974$   $Ti_2^{7+}$  or  $Ti^{3+} \cdot mTi^{4+(m>1)}$  are formed in the systems of alternating copolymerization, which show high selectivity but different activity. A relationship was detected between the ratio Al/Ti, titanium complex "life expectancy" and the effectiveness and selectivity of the alternating copolymerization. Tables 4; figures 3; references 5: 3 Russian, 2 Western.

**Structure and Reactivity of Surface Complexes Forming During Oxidation of CO With Oxygen and NO Over Catalysts Based on Activated  $Al_2O_3$**   
*927M0162I Moscow KINETIKA I KATALIZ in Russian Vol 33 No 3 May-Jun 92 (manuscript received 2 Apr 91) pp 611-617*

[Article by M. A. Ismailov, R. B. Akhverdiyev, V. S. Gadzhikasumov, V. A. Matyshak, Institute of Petrochemical Processes imeni Yu. G. Mar'edaliyev, Azerbaijan Academy of Sciences, Baku; Institute of Chemical Physics imeni N. N. Semenov, Russian Academy of Sciences, Moscow; UDC 541.128.13: 542.943.7:546.262.3-31:541.183:541.124:543.422]

[Abstract] Copper containing catalyst systems are capable of supporting reactions of CO with NO already at room temperature yielding  $N_2O$  and  $CO_2$ . With temperature elevation the reaction rate increases but the  $N_2O$  component of the product decreases, while the  $N_2$  fraction is increased. In the present work the structure and reactivity of carbonyl, carboxylate and nitrate complexes formed on the surface of activated  $Al_2O_3$  catalyst containing Co, Ni and Cu ions was investigated using IR spectroscopy "in situ". It was shown that the rate of carbonyl complex conversion was identical with the rate of the formation of carbon dioxide, while the conversion of carboxylate complexes was lower by three orders of magnitude. On the basis of these findings, the authors concluded that oxidation of CO and the reaction of CO with NO occurs via an intermediate carbonyl complex. Tables 2; figures 3; references 10: 8 Russian, 2 Western

**Effect of Halides (Cl, Br) on Electronic State of Pt in  $Pt/Al_2O_3$  Catalysts Based on IR-Spectroscopy Data in Diffuse-Scattered Light**

*927M0162J Moscow KINETIKA I KATALIZ in Russian Vol 33 No 3 May-Jun 92 (manuscript received 16 May 91) pp 625-628*

[Article by M. D. Smolikov, A. V. Zaytsev, Ye. V. Zatolokina, A. S. Belyy, V. Yu. Borovkov, V. K. Duplyakin, V. B. Kazanskiy, Institute of Organic Chemistry

imeni N. D. Zelinskiy, Russian Academy of Sciences, Moscow; Omsk Department of Institute of Catalysis, Siberian Department of Russian Academy of Sciences; UDC 541.128.3:541.183:546.92'623'131: 539.194:543.422.4]

[Abstract] The goal of this work was to investigate in detail the effect of halides on the state of platinum dispersed on the surface of  $\gamma-Al_2O_3$  catalyst modified with chlorine or bromine ions. Based on the IR-spectroscopic data in diffuse-scattered light, the authors concluded that chlorine (or bromine) react with platinum forming a surface complex containing up to two halide atoms. After reduction of the catalyst with hydrogen at 823 K the dispersed metal particles can be identified on the surface of  $\gamma-Al_2O_3$  along with divalent platinum ions bound directly to chlorine or bromine ions. The ratio of the halides to platinum in these charged forms is about 2. This probably stabilizes the platinum deposited in ionic form on the aluminum-platinum catalysts. Table 1; figure 1; references 6: 3 Russian, 3 Western.

**Effect of High Temperature Carrier Nature on Physical-Chemical Properties of Cobalt Containing Catalysts**

*927M0162K Moscow KINETIKA I KATALIZ in Russian Vol 33 No 3 May-Jun 92 (manuscript received 25 Jan 91) pp 654-663*

[Article by A. S. Ivanova, O. P. Babushok, A. S. Kalinkin, V. P. Ivanov, A. V. Pashis, Institute of Catalysis, Siberian Department of Russian Academy of Sciences, Novosibirsk; UDC 541.128.3:542.975'973: 542.941:546.73'623'284:539.26]

[Abstract] The goal of this work was to investigate the effect of the nature of high temperature carriers ( $\Xi$ - $a-Al_2O_3$ ,  $MO_2$ - $Al_2O_3$  where M= Si, Zr) and of the conditions of preparation on the structure of the active component of cobalt containing catalysts. It was established that an interaction of the active component with the carrier occurred only in the system  $Co/a-Al_2O_3$  resulting in the formation of cobalt aluminate. Correspondingly, the degree of reduction of this specimen with hydrogen was lowest for low cobalt content (about 5%). When cobalt content was increased to 17-23%, the degree of reduction was about 0.6 and did not depend on the carrier. The average size of cobalt particles decreased in the series:  $a-Al_2O_3$ - $ZrO_2$ - $Al_2O_3$ - $\Xi$ - $a-Al_2O_3$ - $SiO_2$ - $Al_2O_3$ . The metallic cobalt particles are both cubic- and edge-centered and hexagon-densely packed; packing defects were noted in crystalline structure. Overall, the active component of the catalysts containing 12-23% of cobalt consisted of 60% of metallic element. Tables 5; figures 4; references 12: 6 Russian (3 by Western authors) 6 Western (2 by Russian authors).

**Study of Low Temperature Cu-Zn Oxide Catalysts  
Nature**

927M0162L Moscow KINETIKA I KATALIZ  
in Russian Vol 33 No 3 May- Jun 92 (manuscript  
received 4 Mar 91) pp 664-671

[Article by L. M. Plyasova, Institute of Catalysis, Siberian Department of Russian Academy of Sciences, Novosibirsk; UDC 542.973:546.47'56-31:548.313]

[Abstract] According to concepts currently being developed on the state of condensed systems, solid materials, in addition to the crystalline and amorphous state, may also find themselves in a transition - paracrystalline state. This concept of paracrystallinity was used to explain the stability of a developed surface and excellent catalytic properties of Fe, Ni, and Cu promoted with non-reducible oxides, whose clusters appear to be endotactically inserted into the metal lattice work causing paracrystalline distortions. The predecessors of the metals found in paracrystalline state are mixed anionic modified oxides. It appears that the low temperature oxides are in such a paracrystalline state. Indeed, using an example of low temperature ZnO promoted with Cu<sup>2+</sup> and compared to a pure material, it was shown that simple and complex oxides formed at low temperatures existed in paracrystalline state. The range of their thermal stability and degree of paracrystallinity were determined. A possible paracrystalline model was discussed for ZnO with -Cu-O-Cu- tactic clusters. Table 1; figures 4; references 18: 10 Russian (1 by Western authors) 8 Western (2 by Russian authors).

**Effect of Kaoline on Acidity of Industrial  
Aluminum Silicate Cracking Catalyst**

927M0162M Moscow KINETIKA I KATALIZ  
in Russian Vol 33 No 3 May- Jun 92 (manuscript  
received 11 Jul 90) pp 688-690

[Article by R. R. Zagidullin, N. Kh. Valitov, R. N. Gimayev, A. V. Minibayev, R. M. Usmanov, S. G. Prokopyuk, Bashkir State University imeni 40th Anniversary of October, Ufa; UDC 542.973:546.623'284:541.183:543.241.5]

[Abstract] The goal of this work was to investigate the effect of kaoline on the acidity of aluminum silicate cracking catalysts consisting of 0.5% Na<sub>2</sub>O, 40% Al<sub>2</sub>O<sub>3</sub>, 59.5% SiO<sub>2</sub> by the method of gaseous titration with pyridine (adsorption of pyridine at 200, 250, 300, 350, 400°C). The acidity was expressed as a ratio of the moles of adsorbed pyridine to the mass or surface of the catalyst. It was shown that with increased levels of kaoline, the acidity of the catalyst was increased. This was due to higher acidity of kaoline itself and to the kaoline acid centers diffusing towards the surface of the aluminum silicate catalyst. Evaluation of competitive binding of pyridine and isopropyl benzene to the catalyst showed that some isopropyl benzene forms very strong bonds with the catalyst so that pyridine cannot displace it. The principal portion of isopropyl benzene adsorbed

by the catalyst, when heated to 400°, underwent cracking with production of propylene and benzene, both of which were displaced by pyridine. Figures 2; references 5: 3 Russian, 2 Western.

**Synthesis of Vinyl Acetate From Acetylene and  
Acetic Acid. Deactivation of Zinc Acetate Catalyst  
in Reactors With Pseudo Liquified Layer**

927M0162N Moscow KINETIKA I KATALIZ  
in Russian Vol 33 No 3 May- Jun 92 (manuscript  
received 2 Aug 88) pp 691-696

[Article by S. V. Romanchuk, G. A. Kozlova, A. V. Serdyuk, A. M. Akimov, N. V. Motin, Yu. M. Popkov, G. N. Kryukova, D. V. Tarasova, V. A. Makhlin, Scientific Research Physical Chemical Institute imeni L. Ya. Karpov, Moscow; UDC 532.973.2:546.47:547.292:541.128.4:542.91:547.361.2'292]

[Abstract] Synthesis of vinyl acetate from acetylene and acetic acid over zinc acetate catalyst deposited on active charcoal is one of the most widely used industrial methods for production of vinyl acetate. The weakness of this process is in a rapid deactivation of the catalyst. Available data do not give a clear picture of the deactivation mechanism. In the present work catalyst performance was investigated during an active process. The data was used to analyze the reasons for accelerated deactivation of catalysts used in industrial reactors with pseudo liquefied layer. It was shown that the initially high activity of this catalyst was due to the action of zinc acetate which was located in the micro-pores of the carrier. At the first stage of deactivation the micro-pores become blocked by the condensation products and finally the deactivation is increased because zinc acetate migrates into the macro-pores and crystallizes out. In the reactors with pseudo liquefied layer this process is intensified because the fine particles of the catalyst are washed out of the reactor. Additional reasons include different distribution of the concentration and temperature fields in these reactors. Different content of acetic acid in the concentration fields could be yet another reason for deactivation. Figures 2; references 18: 6 Russian, 12 Western.

**Deactivation of Zinc Acetate Catalyst For  
Synthesizing Vinyl Acetate From Acetylene and  
Acetic Acid**

927M0162O Moscow KINETIKA I KATALIZ  
in Russian Vol 33 No 3 May- Jun 92 (manuscript  
received 20 Apr 90) pp 697-703

[Article by G. A. Kozlova, R. S. Dulina, M. M. Soderzhinova, D. V. Tarasova, A. K. Avetisov, Scientific Research Physical Chemical Institute imeni L. Ya. Karpov, Moscow; UDC 541.128.3:542.91:547.361.2'292:546.47'26:542.978]

[Abstract] In continuation of their studies on deactivation of zinc acetate catalysts, physical and mathematical

modelling of the deactivation process was performed. The effect of the composition of the reaction medium and temperature on the deactivation rate was studied along with physical-chemical properties of the catalyst and the carrier. In this work fresh industrial catalyst from a reactor with pseudo-liquefied layer was used, as well as material taken out at specific times and a totally spent catalyst. It was shown that catalyst deactivation was related to the surface of the carrier which was changing with the formation of condensation products. The similarity of processes leading to catalyst deactivation was observed whether they were run in a laboratory or in an industrial reactor. Table 1; figures 4; references 7: 2 Russian, 5 Western.

### **Ion-Radical Mechanism of Catalytic Reactions of Hydrocarbons**

*927M0163A Moscow NEFTEKHIMIYA in Russian Vol 32 No 3, May-Jun 92 (manuscript received 14 Nov 91) pp 195-199*

[Article by M. V. Vishnetskaya, B. V. Romanovskiy, Moscow State University imeni M. V. Lomonosov; UDC 541.128]

[Abstract] Catalytic reactions of hydrocarbons are analyzed usually in a framework of carbonium ion mechanisms. The initiators of the catalytic reactions are acidic proton centers on their surfaces. Along with such acidic centers, oxidative centers exist on the surface of aluminum-silicate systems. In present work cation radical mechanisms were discussed of various hydrocarbon reactions on solid oxides with both acidic and oxidative centers. This is based on the concept of generating cation radicals by a single electron oxidation of catalytic molecules followed by fragmentation of the original particles into cations and radicals which then initiate either ionic or radical processes. Specifically, the splitting reactions and formation of C-C and C-H bonds in hydrocarbon molecules were analyzed, the direction of which was found to be dependent on the acidity of the catalytic surface. The cracking of hexanes over non-acidic forms of zeolites leads to typical radical route products; cracking of cumene on alkaline zeolite forms gives products formed by either the radical or the ionic route, while strongly acidic zeolite leads to the ionic route reaction only. References 11: 8 Russian (1 by Western author), 3 Western.

### **Synthesis of High Molecular Weight Phosphine Ligands for Catalysts of Homogeneous Reactions**

*927M0163B Moscow NEFTEKHIMIYA in Russian Vol 32 No 3, May-Jun 92 (manuscript received 9 Jan 91) pp 200-207*

[Article by N. S. Imyanitov, V. A. Rybakov, S. B. Tupitsyn, V. I. Gorchakova, All Union Scientific Research Institute of Petrochemical Processes; All Union Scientific Research Institute of Petrochemistry, St. Petersburg; UDC 661.7 + 678.8]

[Abstract] The obvious advantages of homogeneous complex metal catalysts become somewhat limited in situations where it is difficult to separate the products from the components of the catalytic system. One of a more promising methods for separation of homogeneous catalysts is based on ultrafiltration, but this method can only be used when molecular dimensions of the catalytic components exceed those of the reagents and reaction products. In an attempt to obtain such components, phosphine polymers were synthesized by bromination of polystyrene, polyvinyl chloride and polychloroprene with lithium diphenylphosphide. The latter was obtained from metallic lithium and triphenylphosphine. It was noted that during such reactions, partial destruction of macromolecules occurred. Addition of diphenylphosphine to polybutadiene was achieved when the reaction was initiated by azo-di-isobutyronitrile. Using  $\text{HRh}(\text{CO})(\text{OPh})_3 + \text{PPh}_3$  or  $\text{Rh}_4(\text{CO})_{12}$  as the catalyst made it possible to run the homogeneous hydrogenation of the double bonds in the above products. These phosphorus containing polymers were then used in hydroformylation reaction. The large ligands enabled the separation of the dissolved metal complexes from the reaction products by means of ultrafiltration. Tables 4; references 20: 8 Russian (2 by Western authors), 12 Western.

### **Catalytic Hydrogenation of Phenanthrene in a Carbon Monoxide-Water System**

*927M0163C Moscow NEFTEKHIMIYA in Russian Vol 32 No 3, May-Jun 92 (manuscript received 1 Jan 91) pp 215-219*

[Article by M. I. Baykenov, V. A. Khrupov, M. G. Meyramov, B. T. Yermagambetov, A. Ya. Chen, S. D. Pirozhkov, A. L. Lapidus, Institute of Organic Synthesis and Carbon Chemistry, Kazakhstan SSR Academy of Sciences, Karaganda; Institute of Organic Chemistry, Russian Academy of Sciences; UDC 665.547.677]

[Abstract] The goal of this work was to investigate the hydrogenation kinetics of phenanthrene in presence of an iron sulfide catalyst, carbon monoxide and steam. The catalyst consisted of a 2:1 mixture of FeCr and pyrrhotite. Experimental results agreed adequately with those calculated from a mathematical model. High effectiveness of the binary catalytic system FeCr-pyrrhotite was related to the ability of catalytic amounts of pyrrhotite to activate hydrogen and the reaction of iron oxide ( $\alpha\text{-Fe}_2\text{O}_3$ ) with  $\text{H}_2\text{S}$  leading to the formation of an active sulfide form. Tables 2; figures 2; references: 3 (Russian).

### **Oxidative Dehydrogenation of Alkylnaromatic Hydrocarbons With Sulfur Dioxide Over Aluminum Oxide Catalysts**

*927M0163D Moscow NEFTEKHIMIYA in Russian Vol 32 No 3, May-Jun 92 (manuscript received 5 Nov 91) pp 220-224*

[Article by I. P. Belomestnykh, N. N. Rozhdestvenskaya, G. V. Isagulyants, Institute of Organic Chemistry imeni

N. D. Zelinskiy, Russian Academy of Sciences, Moscow;  
UDC 542.941.8:542.943:547.534.1:546.224.3.1]

[Abstract] Experimental results were reported of oxidative dehydrogenation of ethyl benzene, isopropyl benzene and diphenyl ethane over V, Mo, Cr and W oxides deposited on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the presence of SO<sub>2</sub>, - the hydrogen receptor. The catalytic activity of the metal oxides used decreased in the following order in respect to their dehydrogenation activity in presence of SO<sub>2</sub>: V<sub>2</sub>O<sub>5</sub> > MO<sub>3</sub> > Cr<sub>2</sub>O<sub>3</sub> > WO<sub>3</sub>. The hydrocarbons used exhibited the following reactivity: diphenyl ethane > ethyl benzene > isopropyl benzene. The use of SO<sub>2</sub> assured high conversion rate and selectivity in synthesis of styrene. Tables 4; figure 1; references 9: 6 Russian, 3 Western (1 by Russian authors).

### Carbonylation of Aryl Iodides in Presence of Palladium Catalyst With Oligomer Ligands

927M0163E Moscow NEFTEKHIMIYA in Russian  
Vol 32 No 3, May-Jun 92 (manuscript received  
24 Oct 91) pp 229-234

[Article by E. A. Karakhanov, Ye. A. Runova, Ye. B. Neymerovets, G. V. Berezkin, L. E. Rozantseva, Moscow State University; UDC 542.91:547.259.8]

[Abstract] In recent years considerable attention was generated in the area of the so called hybrid catalysts which combine high activity and specificity with ease of separation from the reaction medium and possible repetitive use. This field was expanded with introduction of soluble polymers. The goals of this work was to obtain palladium catalyst with oligomer polyethylene ligands and to investigate its activity and the potential for repetitive use in carbonylation of aromatic halides. It was shown that bis(polyethylenediphenylphosphine)palladium (II) chloride is one of such effective catalysts. Optimal reaction conditions were studied on a model compound - benzene iodide. Using this catalyst, several substituted aryl iodides were carbonylated at 100° C in o-xylene solution and at atmospheric pressure of carbon monoxide. The following series of diminishing reactivity was established: p-iodotoluene > m-iodotoluene > benzene iodide > o-iodobenzoic acid > p-iodoanisol > nitroiodobenzene > o- iodotoluene > o-iodocarboxybenzene >> o-nitroiodobenzene. Figures 4; references: 5 (Western, 1 by Russian authors).

### Reforming of Benzene Fractions and Gaseous Condensates on Zeolites

927M0163F Moscow NEFTEKHIMIYA in Russian  
Vol 32 No 3, May-Jun 92 (manuscript received  
3 Oct 91) pp 243-249

[Article by V. G. Stepanov, G. P. Snytnikova, K. G. Ione, Institute of Catalysis, Siberian Department of Russian Academy of Sciences, Novosibirsk; UDC 665.73/753]

[Abstract] Experimental results were reported on systematic investigations of the performance of zeolite based catalyst IK-30 in the so called "zeoforming" process of direct distillation benzene fractions and gaseous condensates from different origins. The yield and the composition of the products obtained were analyzed. The IK-30 catalyst consisted of 70% of modified zeolite ZSM-5 and 30% Al<sub>2</sub>O<sub>3</sub>. This process yielded products with lower sulfur content and higher components with high octane. Temperature increase led to increased yield of gaseous products and lower content of liquids. Pressure changes showed a complicated effect and optimization of the conditions was recommended for specific products desired. Overall, the yield and composition of the benzene products depended on the starting materials and on the reaction conditions used; the gaseous products, as a rule, depend only on the reaction conditions. Tables 2; figures 5; references: 4 (Russian).

### Conversion of Methane and Ethane With Carbon Dioxide Over Mn- Containing Catalyst

927M0163G Moscow NEFTEKHIMIYA in Russian  
Vol 32 No 3, May-Jun 92 (manuscript received  
4 Apr 91) pp 250-254

[Article by A. Kh. Mamedov, S. R. Mirzabekova, Sh. A. Nuriyev, V. S. Aliyev, Institute of Petrochemical Processes, Azerbaijan Academy of Sciences, Baku; UDC 547.213:542.941.8]

[Abstract] Reactions of C1-C<sub>2</sub> hydrocarbons with carbon dioxide were studied in presence of Ni- and Mn-containing catalysts. The effect of the catalyst composition and of the nature of alkanes on the yield and composition of the products obtained was elucidated. The reaction occurs at about 870° on the surface of the reduced MnO with the formation of CO and H<sub>2</sub> in case of methane and C<sub>2</sub>H<sub>4</sub> and CO in case of ethane. In both cases CO<sub>2</sub> is reduced to CO. The absence of metallic and carbide phases makes it possible to run stationary reactions without accumulation of carbon precipitates. Modified with chromium, the Mn surface can be reoxidized with CO, resulting in an increased selectivity of the conversion of ethane to ethylene. At the optimal composition the catalyst contained 5.5% Cr and 17% Mn. Table 1; figures 2; references 14: 13 Russian, 1 Western.

**Effect of Medium Polarity on Aggregate Stability and Electrophoretic Deposition of Suspensions of High Temperature Superconductors**

927M0147B Moscow KOLLOIDNYY ZHURNAL  
in Russian Vol 54 No 1, Jan-Feb 92 (manuscript  
received 19 Apr 91) pp 21-25

[Article by V. G. Bedenko, T. N. Nichikova, B. Ye. Chistyakov, N. B. Kalinin, T. P. Gorshkov, A. K. Shikov, All Union Scientific and Design Institute of Surfactive Substances, Shebekino; All Union Scientific Research Institute of Inorganic Materials, Moscow; UDC 5373.363 + 541.18:537 + 541.18.04]

[Abstract] To obtain desired thickness of films from superconducting materials such as yttrium or bismuth ceramics, the method of electrophoretic precipitation of finely dispersed particles from non-aqueous suspensions is used. Experimental data were reported on the effect of the polarity of the dispersion mixture on the formation of electrophoretic films and the aggregate stability of the suspension of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  and  $\text{Bi}_4\text{Sr}_3\text{Ca}_x\text{Cu}_4\text{O}_y$ . It was shown that a decrease in the polarity of the medium (methanol-isopropanol-butanol-undecanol) resulted in a decrease of the electrokinetic potential and the aggregation of Yt and Bi ceramic particles due to decreased electrophoretic mobility of these particles resulting from increased viscosity of the medium and lower  $\xi$ -potential of the particles. Thus, to obtain stable suspensions of high temperature superconducting materials designed for the formation of electrophoretic covers, polar media must be used with dielectric permeability of at least 18. Figures 5; references 17: 11 Russian, 6 Western.

**Flow Theory of Colloid Systems With Fractal Structure**

927M0147C Moscow KOLLOIDNYY ZHURNAL  
in Russian Vol 54 No 1, Jan-Feb 92 (manuscript  
received 30 Sep 91) pp 91-96

[Article by I. Ya. Ladyzhinskiy, G. N. Uryeva, Ya. Mevis, N. B. Uryev, Institute of Physical Chemistry, USSR Academy of Sciences, Moscow; Institute of Chemical Physics, USSR Academy of Sciences, Moscow; Louvain Catholic University, Belgium; UDC 541.182 + 539.37]

[Abstract] Gel viscosity was measured in a wide range of shift velocities; the gel was formed by lyophobic mono-dispersed spherical quartz particles at a 2.5 volume-% concentration. It was shown that this viscosity decreased 10<sup>9</sup>-fold when the shear stress  $\sigma$  exceeded the critical value  $\sigma_c$ . The viscosity values  $\eta_1$  and  $\eta_2$  in the range studied were practically independent of  $\sigma$ . The theoretically calculated  $\eta_1$ ,  $\eta_2$  and  $\sigma_c$  values based on the concepts of fractal structure of dilute aggregates and gels, agreed with the experimentally determined ones. A conclusion was reached that at  $\sigma=\sigma_c$  the system should not be homogeneous, but laminated into two homogeneous phases characterized by  $\eta_1$  and  $\eta_2$  viscosities and shift

velocities  $\sigma/\eta_1$  and  $\sigma/\eta_2$ . Figures 2; references 21: 6 Russian (2 by Western authors), 15 Western.

**Flow Mechanism of Colloidal Systems With Fractal Structure in a Dynamic Mode**

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in Russian Vol 54 No 1, Jan-Feb 92 (manuscript  
received 2 Oct 91) pp 97-99

[Article by I. Ya. Ladyzhinskiy, G. N. Uryeva, Ya. Mevis, N. B. Uryev, Institute of Physical Chemistry, USSR Academy of Sciences, Moscow; Institute of Chemical Physics, USSR Academy of Sciences, Moscow; Louvain Catholic University, Belgium; UDC 541.182 + 539.37]

[Abstract] The elasticity modulus  $G'$  and modulus of losses  $G''$  were determined experimentally for a colloidal gel of spherical  $\text{SiO}_2$  particles as a function of the amplitude of the periodic shear deformation. In the preceding paper an idea was proposed of a coexistence of solid- and liquid like phases during the flow of colloidal systems with fractal structure. This concept of a split into a solid- and liquid like phases was used to explain experimental data obtained in present study; it was not contradictory to theoretical considerations. It could be assumed that the concept of two phases is not just a descriptive method but a reflection of the actual state. The theory is suitable to explain the mechanism of transition and to relate the transition characteristics to the structural characteristics of the system. Figure 1; references 6: 1 Russian, 5 Western.

**Theory of Aggregation in Colloids. Surface Tension at the Interface of Two Colloids**

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in Russian Vol 54, No 2, Mar-Apr 92 (manuscript  
received 9 Nov 89) pp 54-59

[Article by Yu. A. Buyevich, A. Yu. Zubarev, and A. O. Ivanov, Ural State University imeni A. M. Gorky, Yekaterinburg; UDC 532.613.4:541.182.8]

[Abstract] Putting together a theory on the stratification of colloidal phases differing in concentrations of dispersed particles requires determination of the surface tension at the interface of the two phases. While many studies have been made from various points of view, e.g. surface tension between magnetic and non-magnetic colloids, effects of external electrical and magnetic fields on surface tension, a rigorous statistical treatment encounters difficulties caused by the presence of a transitional surface layer between various aggregated states of matter. The thickness of this layer is equal to several inter-particle distances with no thermodynamic limitations, making it impossible to make a strict determination of the thermodynamic quantities within its bulk. Known approximations are based on many intuitive assumptions making it not possible to use them in practical calculations. In the present work the coefficient

of surface tension was approximated on the basis of thermodynamic and statistical consideration of the interfacial surface. From a statistical physics standpoint, an ensemble of interacting colloidal particles is similar to an ensemble of a gas or liquid molecules, making it possible to use results from the theory of dense gases. In the present work formulas for surface tension at the interface between two colloids, differing only in concentrations of dispersed particles, were derived. References 18: 17 Russian, 1 Western.

#### Colloidal Chemical Properties of Polycomplexes Based on Polyacids and Polyacrylamide

927M0148B Moscow KOLLOIDNYY ZHURNAL  
in Russian Vol 54, No 2, Mar-Apr 92 (manuscript received 24 Apr 91) pp 60- 63

[Article by Ye. V. Vorobyeva, N. P. Krutko, and A. A. Litmanovich, General and Inorganic Chemistry Institute, Minsk; UDC 541.64+49]

[Abstract] Research on interpolymeric complexes, a new class of polymers, has attracted much interest owing to the broad possible applications of these substances. In the present work a study was made of complex formation between polyacrylamide and variously hydrophobic polyacids: polyacrylic, polymethacrylic, and copolymer of methacrylic acid with turpentine terpene. Study of these systems has both theoretical and practical interest since polyacrylamides and polycarboxylic acids are used widely in industry and agriculture as flocculants and emulsion stabilizers during oil production, as well as structure formation in soils. The effects of component ratios on viscosity, pH, and surface tension of aqueous

solutions of the polycomplexes are presented. Also, it was demonstrated that the composition and stability of the complexes are functions of the quantity of hydrophobic groups in the polyacid macromolecule. Figures 2; references 10 (Russian).

#### Spinodal Breakdown in Shear Flowing Colloid

927M0148C Moscow KOLLOIDNYY ZHURNAL  
in Russian Vol 54, No 2, Mar-Apr 92 (manuscript received 26 Sep 91) pp 71- 77

[Article by A. Yu. Zubarev, Ural State University imeni A. M. Gorky, Yekaterinburg; UDC 541.18:536.763]

[Abstract] Spinodal breakdown is the process where a system departs from a state of absolute thermodynamic non-equilibrium. Although general rules governing this process in stationary colloidal and molecular systems have been studied, a complete theory has not yet been formulated. Development of spinodal breakdown in shear flowing suspensions and colloids has several special features associated with the effects of overall non-equilibrium on phase striation and by the change in rheological properties of a suspension during the genesis and separation of dense and thin phases formed during spinodal breakdown. In the present work a theoretical study was made of the kinetics of spinodal breakdown in a colloid involved in shear flow. The effects of the flow rate gradient on the kinetics of spinodal breakdown and the geometric structure of the striating systems were evaluated. Analysis of the change in effective viscosity of the colloid during the course of this process agrees qualitatively with known experimental data. Figures 2; references 24: 12 Russian, 12 Western.

**Effect of Intermolecular Reaction on Sensitivity of Liquid Explosives**

*927M0086B Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 320, No 1, Sep 91 (manuscript received 21 Jun 91) pp 148-150*

[Article by Academician N. S. Yenikolopyan, L. V. Larionov, P. P. Babenko, A. B. Sergiyenko, G. I. Syrenkov, and Ye. L. Larionova, Synthetic Polymers Institute; Chemistry and Mechanics SRI (Central), Moscow; UDC 662.215]

[Abstract] Widespread use of explosives in both science and the national economy brought urgency to the development of methods for controlling the physical characteristics of these substances, especially the lowering of sensitivity. At the present time explosive sensitivity is most often lessened by addition of phlegmatizers or eutectic melts. However, these method's are not suitable for liquids such as nitroglycerine. In the present work impact tests demonstrated the feasibility of adding an electron charge transfer complex. Liquid nitroglycerine itself served as an electron acceptor to which was added varying amounts of  $\gamma$ -butyrolactone or imidazole as electron donor to form the complex. It is postulated that the same approach may used for solid explosives since a great number of solid adducts of aromatic nitrocompounds having donor electrons are available. Figures 2; references 5 (Russian).

**Comments on V.A. Mikhelson's Detonation Wave Theory**

*927M0133B Moscow KHIMICHESKAYA FIZIKA in Vol 11 No 2, Feb 92 (manuscript received 2 Jul 91) pp 248-257*

[Article by N. Manson, National Mechanics and Aeroengineering Higher Educational Institution, Poitou, France; UDC 534.222]

[Abstract] A comparison of the original version (1890) of V.A. Mikhelson's detonation wave theory and his modified theory (1920) reveals that Mikhelson actually presented the essence of what is now referred to as the Chapman-Jouget theory before Chapman and Jouget did. In the first version of his dissertation (published in Moscow in 1890), Mikhelson set forth the very essence of the now-classical theory of detonation waves. The publications of Chapman (1899), Jouget (1905-1917), and Crussard (1907) contain a great many details that essentially just refine the theory originally presented by Mikhelson's dissertation in 1890. When Mikhelson prepared the second version of his dissertation, which was published in 1930, he was not acquainted with the works of Chapman, Vieille, Jouget, or Crussard. Furthermore, the revisions and additions that Mikhelson included in his 1930 publication are only of secondary interest. In view of these facts, historical reviews of the problem of detonation and bibliographies on the theory of detonation and detonation waves should refer to Mikhelson's first version of the said theory rather than to his second

version. A concise outline of the classical Chapman-Jouget theory of detonation waves is appended. Figures 4; references 23: 3 Russian, 20 Western.

**Concentration Limits of Flame Propagation in Gas-and-Air Mixtures Under Reduced Pressures**

*927M0133C Moscow KHIMICHESKAYA FIZIKA in Vol 11 No 2, Feb 92 (manuscript received 20 Mar 91) pp 258-263*

[Article by A.Ya. Korolchenko, S.G. Tsarichenko, Yu.N. Shebeko, P.N. Kozlov, A.V. Trunov, V.P. Mokryshev, and V.G. Shamoin, All-Union Scientific Research Institute of Fire Protection; UDC 614.841]

[Abstract] The authors of the study reported herein examined the concentration limits of flame propagation in gas-and-air mixtures at reduced temperatures. Specifically, they determined the flame propagation concentration limits of mixtures of methane, carbon oxide, hydrogen, and nitrogen with air at room temperature in the range of pressures from 0.5 to 100 kPa. The experiments were conducted in two experimental units. The first unit had a reaction chamber in the form of a closed horizontal cylinder with an inner diameter and length of 500 mm and with one transparent end made of acrylic plastic. It had a volume of 100 dm<sup>3</sup>. The reaction chamber of the second unit also had a volume of 53 dm<sup>3</sup>. The latter reaction chamber was in the form of a closed vertical cylinder with an inner diameter of 300 mm and a height of 800 mm. It contained a small transparent window. The gas mixtures were prepared in a high-pressure mixer and were fed from the mixer into the reaction chamber after it had first been evacuated. During the experiments, four different sources were used to initiate combustion: a high-voltage spark with an energy of about 1.5 J (discharge interval, 2 mm); an arc discharge with an energy of about 30 J (discharge interval, 4 mm); a burnable Nichrome wire 4 mm long and 0.15 mm in diameter (burn voltage, 42 V; released energy, about 2 J); and a burnable Nichrome wire 10 mm long and 0.3 mm in diameter (burn voltage, 110 V; released energy, about 20 J). Flame propagation was recorded visually. The flame propagation concentration limits of hydrogen were determined by darkening the area in which the experiments were performed. The studies performed established that the lowest limit pressure for methane may reach a value of about 0.5 kPa when an arc discharge with an energy of about 30 J is used to initiate combustion. In the case of the burnable wire, increasing the ignition energy from 2 to 20 J resulted in a nearly twofold reduction in limiting pressure. In cases where the mixture was ignited by an electric discharge, increasing the source's energy from 1.5 to 30 J resulted in a decrease in limiting pressure from 6 to 0.5 kPa. The studies further established that the limiting pressure is determined not by the volume of the reaction vessel but rather by the characteristics of the ignition source. The lower concentration limit of flame propagation was decreased and the upper concentration limit increased when the pressure was reduced from 100

to 15 kPa. A model borrowed from a 1976 publication by Smoot et al. was used as a basis for calculating the normal combustion rate of depleted methane-and-air mixtures at reduced pressures. A theoretical interpretation of the study results is also provided. Figures 5; references 19: 8 Russian, 11 Western.

### The Detonation Mechanism of Self-Excited Wave Phenomena in Cryochemical Solid-Phase Processes

927M0133D Moscow KHIMICHESKAYA FIZIKA  
in Vol 11 No 2, Feb 92 (manuscript received  
21 May 91) pp 264-268

[Article by D.P. Kiryukhin, P.S. Mozhayev, and V.V. Barelko, Chemical Physics Institute, Russian Academy of Sciences, Chernogolovka; UDC 517.9:541.64+15]

[Abstract] Previous studies of self-excited wave phenomena in solid-phase cryochemical processes have focused on a model that has in turn focused on the leading role played by the steep temperature gradients that arise at the front of the traveling transformation wave. These temperature gradients are caused by the breakdown and scattering of the layer of reagents adjacent to the front and by the chemical activity stimulated in it on account of this effect. This mechanico-thermal mechanism is not the only possible mechanism of self-excited wave phenomena in cryochemical solid-phase processes, however. An alternative mechanism is also possible. It is based on the role of the change in density of matter during the course of the reaction—a factor that may be yet another physical reason for the formation of a stress field in the wave front that destroys the solid matrix. In light of these facts, the authors of the study reported herein used the example of a model reaction of the chlorination of butyl chloride to examine the different modes of self-excited wave transformation initiated by local brittle fracture of a solid specimen at low temperatures. A controlled series of measurements of the dependence of heat wave velocity on irradiation dose were performed in cylindrical ampules measuring about 0.8 cm in diameter. The ampules were vertically immersed in a liquid nitrogen bath. This froze the solid solution of reagents (chlorine and butyl chloride in a 1:3 molar ratio) that had been placed into the ampules. After the reagents had frozen, the specimen was subjected to  $\gamma$ -radiolysis at 77 K. A transformation wave was initiated by local brittle fracture of the specimen by feeding the pulse of an electric discharge of specified energy through a wire microheater that had been frozen into the upper portions of the specimens. The wave's propagation rate was measured on the basis of the time required for the front to pass between copper-constantan thermocouples that had been frozen into the cylindrical specimens along their axes at set distances from one another. These thermocouples enabled the researchers to record both the temporal and spatial information regarding the wave front. The thermocouples used had an inherent thermal inertia of about  $10^3$  seconds. The experiments performed established that under the specific conditions of

transformation wave initiation at irradiation doses  $>2$  kGy, there is a transition from the previously observed mechanically active model of self-excited wave propagation to a shock-generating process that is self-sustained on account of a change in density of the solid matter during the course of its transformation and that is similar in nature to a detonation phenomenon. At dose levels of 2 kGy or less the velocities of waves triggered from above and below were nearly the same. At doses above 2.0 Gy, initiation from above resulted in a wave that changed velocity monotonically, increasing to velocities not exceeding 8 cm/s. When the waves were initiated from below, the velocity of the wave jumped after some threshold dose value (3.0 to 4.0 kGy) was passed and then increased by more than an order of magnitude, reaching 8 m/s at a dose of 110 kGy. The structure of the front also changed significantly in a manner confirming that the front of a shock-generated wave depends not on temperature gradients but rather on changes in density. The detonation mechanism presented is said to also be entirely suitable for use in describing fast self-excited wave modes in the area of phase transformation processes occurring in solids (such as in the case of decays of vitreous states into polycrystalline states). Figures 2; references 9: 8 Russian, 1 Western.

### Stability of Laminar Flame in Gas

927M0133E Moscow KHIMICHESKAYA FIZIKA  
in Vol 11 No 2, Feb 92 (manuscript received  
25 Jul 91) pp 269-284

[Article by O.A. Borisova, B.V. Lidskiy, and B.V. Novozhilov, Chemical Physics Institute imeni N.N. Semenov, Russian Academy of Sciences, Moscow; UDC 536.46]

[Abstract] There are two aspects to theoretical research on the stability of a plane stationary flame in gas in relation to two-dimensional disturbances: the hydrodynamic aspect and the heat-diffusion aspect. Separating the problem of the stability of a laminar flame in gas is of course artificial because hydrodynamics, kinetics, and transfer processes are all interconnected and affect one another during the evolution of a disturbance over time. The need to consider both sides of the problem was acknowledged over 10 years ago; however, high-speed electronic computers were needed before both the hydrodynamic and heat-diffusion aspects of the stability of a laminar flame in gas could be formulated into a single problem. The authors of the study reported herein worked within the framework of a simple model of chemical transformation in a linear approximation to develop a method for numerical analysis of the problem of the stability of a plane laminar flame in relation to two-dimensional disturbances. The proposed method gives consideration to hydrodynamics, kinetics, and transfer processes (including viscosity). Several examples illustrating the use of the new method are presented. The process of finding a stationary solution to the problem and the stability of stationary solutions are discussed. After analyzing the stability of the solutions

resulting from the use of their proposed method against the background of the established practice of separating hydrodynamic and heat-diffusion effects, the authors reach the following conclusions: 1) despite all its artificiality, the practice of separating instability into heat-diffusion and hydrodynamic instability still makes a certain amount of sense inasmuch as stability losses may occur both when  $\text{Im } \omega$  is and is not equal to 0; 2) the value of  $\chi$  at which the combustion mode will begin to be absolutely stable at all values of  $\beta$ ,  $\alpha$ , and  $\text{Le}$  will always be found; and 3) increasing  $\text{Le}$  expands the region of heat-diffusion stability and will have the reverse effect on the region of hydrodynamic stability. Figures 5; references 10: 8 Russian, 2 Western.

### Detonation Capability of Fine-Grained Pyroxylin Powders

927M0133G Moscow KHIMICHESKAYA FIZIKA  
in Vol 11 No 2, Feb 92 (manuscript received  
30 Oct 90) pp 293-299

[Article by V.F. Martynyuk, A.A. Sulimov, S.V. Chekanov, G.B. Brauer, and M.K. Sukoyan, Chemical Physics Institute imeni N.N. Semenov, Russian Academy of Sciences, Moscow; UDC 535.529+662.215.1]

[Abstract] The authors of the study reported herein examined the detonation capability of fine-grained pyroxylin powders in paper and strong steel jackets. Specifically, they studied the effects that the properties of the jacket, the initiation method, and the size of the powder grains have on detonation parameters. Cylindrical granules of the pyroxylin powders VU, VT, VTM, and 4/1 were used. The powders had respective grain sizes of 0.6, 0.8, 1.1, and 1.7 mm and channel diameters of 0.1, 0.13, 0.15, and 0.25 mm. The granular charges

used had densities of 850 to 950 kg/m<sup>3</sup>. Detonation was initiated by shock waves of different amplitudes that were introduced through an inert enclosure, as well as by the method of "explosive initiation," according to which detonation was excited by the layer of an elastic explosive that was brought into contact with the powder and with a duralumin jacket. Either the combination of a ZhFR-3 photographic recorder and ionization sensors or the optic fiber method was used to measure the process propagation rate in the individual experiments. The critical diameters and critical pressures of initiation of normal and low-speed detonation were measured. The experiments performed established that in charges measuring between 35 and 56 mm in diameter, either normal or low-speed detonation may occur in charges in a paper jacket depending on the power of the initiator. The critical diameter of the propagation of normal detonation was found to be 30 mm, and in that range normal detonation was propagated stably at charge lengths of 20 calibers. Weak initiation was found to result in low-speed processes. In general, the critical diameters of normal and low-speed detonation were found to increase as grain size increased. At the same time, the critical pressures of the initiation of normal and low-speed detonation were found not to depend on grain size in the particle size range studied. In both paper and strong steel jackets, low-speed processes were propagated over large distances at a virtually constant velocity. In such cases the nature of the development of low-speed detonation depended on granule size and phlegmatization of the surface layer: Increases in grain size and phlegmatization of the surface were both found to retard development of the process. The experiments further established that in the case of the powder 4/1 in a strong steel jacket with an inner diameter of 15 mm, process speed is dictated by initiation conditions. Figures 6; references 8: 6 Russian, 2 Western.

**Electrochemical Treatment of Surface of Alloy Steels—A New Method of Increasing Their Corrosion Resistance**

927M0122A Yerevan ARMYANSKIY KHIMICHESKIY ZHURNAL in Russian Vol 44 No 6, Jun 92  
(manuscript received 26 Jun 90) pp 344-350

[Article by V.N. Ovchyan, A.R. Oganesyan, L.M. Avanesova, S.Ye. Agababyan, and Ts.R. Stepanyan, General and Inorganic Chemistry Institute, Republic of Armenia Academy of Sciences, Yerevan; UDC 620.193.423]

[Abstract] The idea of making use of the ability of certain metals and alloys to become passivated under specified conditions has been recognized as a promising direction for exploring new ways of protecting the said metals and alloys against corrosion. Often surface products that are themselves the result of corrosion serve to protect a metal against subsequent oxidation. In other words, under certain conditions, metals and alloys acquire corrosion resistance thanks to the formation of insoluble (or sparingly soluble) oxide, hydroxide, or salt films. The authors of the study reported herein have made use of this principle in developing a new method for increasing the corrosion resistance of alloy steels based on electrochemical surface treatment in silicate alkaline solutions. Their use of silicate alkaline solutions as opposed to purely alkaline solutions was based on the results of preliminary studies confirming that metal in a passive state has a much lower tendency to corrode when in a silicate alkaline solution. In essence, the proposed preliminary electrochemical treatment method includes successive potentiostatic polarization of steels in silicate alkaline solutions, first at a potential of -1.05 to -0.95 V and then at potentials of 0.60 to 0.65 and -0.15 to -0.25 V. A solution containing 10 to 15 g/l NaOH with a silicate modulus of (0.5-1):1 was used as the silicate alkaline solution. The treatment process was conducted at a temperature of 70 to 80°, with each stage lasting 15 to 45 minutes. Thanks to the new electrochemical procedure, the alloy steels treated developed an extremely high corrosion resistance in sulfuric acid (up to 50%) and in hydrochloric acid (up to 5%). Some of the steel specimens treated maintained their corrosion resistance in 2% HCl for up to 27 days and for up to 200 hours in 5% HCl. In 10% solutions of  $H_2SO_4$ , some of the specimens maintained their corrosion resistance for up to 2 years. Figures 2, tables 2; references 13: 12 Russian, 1 Western.

**Electrochemical Synthesis and Investigation of Benzoylacetone and Dibenzoylmethanate Complexes of Cobalt (II)**

927M0123A Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 37 No 1, Jan 92 (manuscript received 19 Jul 91) pp 68-71

[Article by N.N. Kostyuk, V.L. Shirokiy, I.I. Vinokurov, T.A. Dik, D.S. Umreyko, and A.A. Erdman, Applied

Physics Problems Scientific Research Institute imeni A.N. Sevchenko and Physical and Organic Chemistry Institute, Byelorussian Academy of Sciences; UDC 546.07.73+541.118+541.135]

[Abstract] The authors of the study reported herein examined the possibility of using electrochemical synthesis as a way of producing chelate complexes of cobalt with the ligands 1-phenyl-1,3-butanedione (benzoylacetone) and 1,3-diphenyl-1,3-propanedione (dibenzoylmethane). The electrolysis was implemented with a direct current at room temperature in a diaphragmless cell with a volume of 70 ml. A cobalt anode was placed in the center of the cell and surrounded by a cylindrical cathode made of nickel foil. A 0.1 N solution of lithium chloride in ethanol was used as an electrolyte. The concentration of  $\beta$ -diketone in the 30-ml solution amounted to 0.5 mol/l. A current density of 8 to 10 mA/cm<sup>2</sup>, voltage of 3 V, and electrolysis time of 3.5 hours were used. The resultant compounds were analyzed to determine their carbon and hydrogen contents. A Specord IR-75 spectrophotometer, V-630 cathetometer, and MX-1300 mass spectrometer were used during the analysis process. The elemental analysis and spectroscopy studies performed confirmed that electrolysis of benzoylacetone [BA] and dibenzoylmethane [DBM] in ethanol on a cobalt anode results in the formation of the respective complexes  $[Co(C_2H_5OH)(BA)_2]$  and  $[Co(DBM)_2 \cdot 3C_2H_5OH]$ . Thermolysis of the said compounds was demonstrated to result in the formation of  $[Co(BA)_2]$  and  $[Co(DBM)_2]$ , respectively. Specifically, holding  $[Co(C_2H_5OH)(BA)_2]$  in an inert atmosphere at 398 K resulted in a 9.6% mass loss, which is close to what would result from the splitting off of 1 mole of ethanol (i.e., 10.8%). Heating  $[Co(DBM)_2 \cdot 3C_2H_5OH]$  for 2 hours at 348 K resulted in a mass loss of 7.18%, which corresponds to the splitting off of 1 of 3 moles of ethanol (7.15%) and thus in the formation of  $[Co(C_2H_5OH)_2(DBM)_2]$ . Subsequent heating of the latter to 405 K results in a 22.4% loss of mass after 2.5 hours and thus in the formation of  $[Co(DBM)_2]$ . Figure 1; references 4: 3 Russian, 1 Western.

**Extraction, Spectrophotometric, and Electrochemical Characteristics of Heteroligand Complexes of Platinum (II) and Palladium (II) With Substituted 8-Mercaptoquinolines and Triphenylphosphate**

927M0123B Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 37 No 1, Jan 92 (manuscript received 25 Jun 91) pp 100-106

[Article by S.V. Mashkina, N.A. Ulakhovich, G.K. Budnikov, Kazan State University; UDC 543.253]

[Abstract] The authors of the study reported herein used the methods of spectrophotometry, classical polarography, and alternating-current and cyclic voltammetry to

study the heteroligand complex formation and extraction of 8-mercaptopquinolines of platinum and palladium substituted into a triphenylphosphate melt. Specifically, the researchers synthesized and studied 8-mercaptopquinolines containing the substituents R = 2-CH<sub>3</sub>-, 2-C<sub>6</sub>H<sub>5</sub>-, 2-CH<sub>3</sub>S-, 4-C<sub>6</sub>H<sub>5</sub>-, 5-CH<sub>3</sub>S-, 5-C<sub>6</sub>H<sub>5</sub>, 5-C<sub>6</sub>H<sub>5</sub>S-, 7-C<sub>6</sub>H<sub>5</sub>O-, and 7-C<sub>6</sub>H<sub>5</sub>S-. The purity and individuality of the mercaptopquinolines were controlled by elemental analysis and thin-layer chromatography. Dimethylformamide was used as a solvent during the electrochemical studies. An SF-26 spectrophotometer, PU-1 polarograph, TsLA PO 5122 model 03 oscillopolarograph, and EV-74 ionograph were used in the studies. The studies performed confirmed that heteroligand complexes are formed when triphenylphosphate is used as a low-melting extractive reagent to extract mercaptopquinolines of platinum and palladium. The studies further established that a substituent in the quinoline ring affects the stability of the resultant adducts. Adding  $\sigma$ -donor substituents was found to result in a decrease in the constant of adduct stability when compared with nonsubstituted chelates, whereas aryl-substituted complexes were found to be characterized by higher adduct formation constants. Additional coordination of the triphenylphosphate molecule functioning as a  $\pi$ -acceptor results in changes in the spectral and electrochemical characteristics of platinum and palladium chelates. The heteroligand complexes discovered may be used in determining platinum and palladium. Specifically, the said complexes may be used for spectrophotometric-extraction determination in cases where the mercaptopquinolate concentration is greater than 10<sup>-5</sup> mol/l and for voltammetric-extraction determination of platinum and palladium in cases where the mercaptopquinolate concentration is between 10<sup>-7</sup> and 10<sup>-3</sup> mol/l. Figures 4, tables 2; references 13: 10 Russian, 3 Western.

### Kinetics of Controlled-Diffusion Electrochemical Reactions in Porous Media by Way of the Example of Lead Dioxide

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in Vol 11 No 1, Jan 92 (manuscript received  
27 Sep 90) pp 135-146

[Article by S.F. Burlatskiy and M.G. Rudenko, Chemical Physics Institute imeni N.N. Semenov, USSR Academy of Sciences, and Chemical Physics Institute imeni N.N. Semenov, USSR Academy of Sciences, Chernogolovka; UDC 541.13]

[Abstract] The authors of the study reported herein conducted a theoretical examination of the kinetics of controlled-diffusion electrochemical reactions in porous media. They based their mathematical analysis on a macrohomogeneous model examined in previous publications (by Turner and Moseley, Simonsson, and Micka and Rousar). According to the said model, an actual electrode is looked upon as a homogeneous medium whose characteristics change along the x-axis but are assumed to remain constant in the plane perpendicular to the x-axis. Working within the framework of an approach developed by Ya.B. Zeldovich, they derived an expression for numerical estimation of the effective depth of the reaction zone. The cases of a constant current and constant concentration at the electrode-electrolyte solution interface were considered separately. Formulas were derived for the distribution of current density and concentration inside the electrode plate. The differences in the discharge process occurring in cases of a thick and thin electrode were analyzed. Specifically, the authors demonstrated that in cases of a constant acid concentration on the surface of a thick electrode ( $L \gg \xi$ ), the concentration of acid will decrease quickly throughout the entire thickness of the electrode. In cases where the electrode is thin ( $L \ll \xi$ ), on the other hand, the change in the acid concentration will be smoother. The results obtained were said to be applicable in describing the operation of a lead storage battery. Figures 6; references 15: 5 Russian, 10 Western.

### Thermal Generation of Ozone in Solids

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in Vol 11 No 2, Feb 92 (manuscript received  
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[Article by A.N. Katushonok and Yu.N. Rufov; Chemical Physics Institute imeni N.N. Semenov, Russian Academy of Sciences, Moscow; UDC 541.183.541.124.16.546.214]

[Abstract] The scientific literature contains reports of the formation of higher-than-equilibrium concentrations of different forms of oxygen when  $O_2$  molecules in mainly an  $X^3\Sigma^-$  state interact with solids. Specifically, the formation and gaseous phase emission of atomic and molecular singlet ( $a^1\Delta$ ) oxygen has been observed and reported. In an effort to expand the circle of solids capable of "generating" singlet  $O_2$ , the authors of the study reported herein attempted to record the formation (thermal generation) of molecules of singlet ( $a^1\Delta$ ) oxygen in other solids by using the techniques of selective chemical detection, optical spectrophotometry, and mass spectrometry. They succeeded in recording the thermal generation on  $\beta$ -bismuth molybdate ( $\beta$ - $Bi_2Mo_2O_9$ ) in air at a pressure of 1 atm. 1,3-Diphenyl-iso-benzo-furan was used as a detection solution. Next, the researchers proceeded to examine the role of the gaseous phase in the ozone generation process. A specimen of  $\beta$ - $Bi_2Mo_2O_9$  heated to 400°C was blown with a helium stream in which the oxygen impurity did not exceed 0.004% (vol). Kinetic curves of ozone generation on  $\beta$ - $Bi_2Mo_2O_9$  in air and helium were plotted. The experiments established that ozone also forms in an oxygen-free atmosphere. The studies further established that a specimen that has operated in helium for an extended period may be partially regenerated by holding it in a flow of air at 300°C for 6 hours. After a specimen was subjected to such regeneration, the ozone emission rate from the entire specimen increased from  $6.8 \times 10^{13}$  to  $1.5 \times 10^{14}$  molecules/s. The observed dependence of the quantity of ozone generation on the mass of the specimen led the researchers to hypothesize that the generated ozone is partially lost in a thick layer of polycrystalline specimen. The experimental effective activation energy of the thermal generation of ozone on  $\beta$ -bismuth molybdate in the temperature interval from 390 to 440°C was determined to equal  $33 \pm 3$  kcal/mol. The authors concluded their report by stating that the formation of ozone observed in other solids is of a purely qualitative nature and confirms only the fact that such ozone formation may play a role in different physicochemical processes at a gas-solid interface, particularly in catalytic reactions. Figure 1; references 10: 4 Russian, 6 Western.

### Ecological Agrochemical Bases for Using Phosphorus Fertilizers

927M0143A Moscow KHIMIZATSIYA SELSKOGO KHOZYAYSTVA No 10, Oct 91 pp 40-45

[Article by O. S. Sdobnikova and B. A. Sushenitsa, All-Union Scientific Research Institute of Fertilizers and Agronomic Soil Science; UDC 631.85]

[Abstract] Simple forms of phosphorus fertilizers, particularly phosphate fertilizer, have repeatedly been shown to exhibit the greatest economic and energetic effectiveness. However, the impurities often found in phosphate fertilizer present a risk of environmental contamination when such fertilizer is used. Cadmium, which is the most dangerous of these impurities, is sometimes found at higher levels (up to 170 mg/kg in Australian fertilizer) in foreign phosphate, as compared to Russian fertilizers (levels of cadmium not greater than 10 mg/kg). Lead levels in Russian phosphate fertilizers are not dangerous. American and Moroccan phosphate fertilizers contain 3-4 times more radionuclides than Russian or Syrian fertilizers. Natural radionuclide content depends on method of preparation as well as source. The highest levels found in Russian fertilizer were in those produced in the Novokokandskiy and Samarkandskiy factories, while the lowest levels were seen in Charzhouskiy factory product. Fluorine levels of 2.1% to 3.9% were observed in phosphate fertilizers, both Russian and foreign. This fluorine may interact with other elements present in soil to produce harmful contaminants which can migrate into agricultural plants. However, since fluorine is a requisite part of human and animal nutrition, it is not advantageous to eliminate it completely from phosphorus fertilizers. Long term experience has demonstrated that indigenous phosphate rock can be used as an effective, safe, and economical fertilizer. In general, poorly soluble forms of phosphorus fertilizer are safer. References 4: Russian.

### Investigation of Chemical Composition of Agroecosystem Components

927M0143C Moscow KHIMIZATSIYA SELSKOGO KHOZYAYSTVA No 10, Oct 91 pp 58-62

[Article by I. B. Savelyev, A. V. Bodrov, and L. B. Astvatsatryan, All-Union Scientific Research Institute of Fertilizers and Agronomic Soil Science; UDC 631.41]

[Abstract] X-ray activation, mass spectrometry with laser and plasma ionization sources, automated liquid and gas chromatography, atomic emission and absorption, biophysical and microbiological methods of analysis are potentially useful in determining the chemical composition of agroecological system components. Non-destructive methods for determining the chemical composition of soil and plants, such as neutron activation, X-ray fluorescence, reflection IR spectrometry, NMR, and EPR are particularly promising. One of the most important current tasks is development of methods, apparatus, automation, and electrification for diagnosing agrobiocenosis state and/or the mineral requirements of crops. Rapid methods and portable automated equipment are desirable, especially for determining nitrate levels. More effort needs to be expended in establishing standards and instrument calibration. The All-Union Scientific Research Institute of Fertilizers and Agronomic Soil Science has developed neutron activation methods for analyzing N, P, K, Mg, Cl, and Si in plants and fertilizers, as well as the soil formation

elements Si, Al, Fe, and Mg. Matrix effects are much lower than found with X-ray fluorescence. Sample preparation requirements limit the productivity of X-ray fluorescence. Using X-ray fluorescence one may determine K, P, Ca, Ti, Mn, Fe, Cr, Ni, and Cu in soil, and K, P, Ca, Cl, Fe, Zn, Cu, and other elements in plants. A modified Dumas method can be employed to measure nitrogen, carbon, and sulfur in soil. Plasma emission spectroscopy can be used in the elemental analysis of soil and plants down to nanogram concentrations of 70 elements.

### **Ecologically Safe Grain Complexes in Light, Chernozem-Poor Soil**

*927M0143D Moscow KHIMIZATSIYA SELSKOGO KHOZYAYSTVA No 10, Oct 91 pp 73-77*

[Article by Ya. T. Kirikoy, M. P. Listova, and L. S. Platonova, All-Union Scientific Research Institute of Fertilizers and Agronomic Soil Science; A. N. Plekhanov, N. M. Belous, F. V. Moiseyenko, S. A. Tudin, A. T. Kurilenko, and M. G. Draganskaya, Novozybkovskiy Department, All-Union Scientific Research Institute of Fertilizers and Agronomic Soil Science; UDC 631.151.2]

[Abstract] Various measures have not succeeded in improving the agricultural productivity of the chernozem-poor zones of Russia. In years with favorable rain levels during the vegetative period, where scientific agriculture is used, light chernozem-poor soil can produce 2500-3000 kg of grain per hectare. With meticulous calculation of soil conditions, use of high-intensity strains, and qualitative fulfillment of agrotechnical requirements, yields can reach 4000-4500 kg/hectare, which is close to the theoretical maximum. By 1995 protein balanced grain based feeds will be possible, due to nitrogen supply optimization and wider use of legumes. One important goal is development of intensive low profile winter rye with decreased amylolytic activity. Improved agronomic monitoring, new strains with greater pathogen resistance and higher yield, better crop rotation, improved methods for corn cultivation and for use of fertilizers with high yield strains, and enhanced ecological monitoring and research, particularly concerning the effects of the Chernobyl reactor accident, are required. Contamination of 20-40 Ci/km<sup>2</sup> has been observed, with individual readings as high as 70 Ci/km<sup>2</sup>. The technological questions associated with agriculture in the contaminated zone require further research and scientific reasoning.

### **Development of Regional Ecologically Safe Grain Complexes**

*927M0143e Moscow KHIMIZATSIYA SELSKOGO KHOZYAYSTVA No 10, Oct 91 pp 84-87*

[Article by M. K. Suleymenov, correspondent member of All Union Academy of Agricultural Sciences imeni V. I.

Lenin, All Union Scientific Research Institute of Grain Cultivation; UDC 631.95:633.1]

[Abstract] The current trend towards mixed and/or rotated cultivation of corn, millet and grass pasture, rather than constant cultivation of grains such as oats or wheat, alternating with fallow periods, has a favorable ecological effect and improves crop yields. Preserving the stubble during postharvest soil treatment assists in water and snow retention. When fallow periods are eliminated, nitrogenous fertilizers can raise yields, and are used in addition to phosphorus fertilizers. In addition to proper methods of physical soil cultivation, herbicides like 2,4-D amine salt and avadex BV are used to combat weeds. Organic fertilizers, maintaining straw in fields during harvest, and optimal crop rotation are used to reduce soil erosion. Proper application of agricultural technology can double wheat, oat, and barley yields. Prediction of the recurrence of pathogens and pests which have five to ten year cycles and improved agricultural machinery, particularly with respect to regional requirements, will be necessary to further increase crop yields.

### **Development of Regional Ecologically Safe Grain Complexes**

*927M0143F Moscow KHIMIZATSIYA SELSKOGO KHOZYAYSTVA No 10, Oct 91 pp 102-105*

[Article by V. F. Sayko, V. I. Gamaley, and A. D. Gritsay, Ukrainian Scientific Research Institute of Agriculture; UDC 577.4; 631.174]

[Abstract] At the Ukrainian Scientific Research Institute of Agriculture yields of 64,000-67,000 kg/hectare have been achieved using 12 tons/hectare of manure, 270-379 kg/hectare NPK fertilizer, and 2.6- 3.9 kg/hectare of pesticides. However, ecological considerations prevent widespread adoption of this regime. Dose optimization, split applications, use of nitrification inhibitors and liquid manure, and rotation with Cruciferae are under study in development of complex agrotechnical measures for ecologically safe crop management. The effect of chemical agents on soil microflora must also be considered. A crop rotation experiment using peas, winter wheat, beets, and barley, without fertilizers, in 1987-1990, was found to cause humus loss and mineralization of 0.06 tons/hectare. This loss was reversed with manure and NPK fertilizer application, without excessive heavy metal contamination. No serious water pollution resulted. Heavy use of NPK fertilizer caused nitrate accumulation in plants, which can be avoided by using an optimal dose. Pesticide residues were not found in the crops. The grains produced were used in a six-month toxicological experiment on white rats, which exhibited no behavioral or morphological changes.

**Synthesis of Binary Rubidium-Gadolinium Phosphates at 350°C**

927M0127B Moscow ZHURNAL NEORGANICHESKOY KHMII in Russian Vol 37 No 5, May 92 (manuscript received) pp 986-990

[Article by A.Yu. Sazhenkov, V.A. Masloboev, V.P. Chaykin, and M.P. Ryskina, Kola Scientific Center, Russian Academy of Sciences, and Institute for the Chemistry and Technology of Rare Elements and Crude Minerals (Apatites); UDC 546.662.35.185]

[Abstract] The authors of the study reported herein studied the reaction occurring in the system  $Rb_2O$ - $Gd_2O_3$ - $P_2O_5$ - $H_2O$  at 350°C. Chemically pure  $Rb_2CO_3$  and  $Gd_2O_3$  and 85%  $H_3PO_4$  (high-purity) were heated to 220-230°C for a day to obtain a homogeneous melt. The furnace temperature was then increased to 350°C, at which point the crystal formation process began. It lasted from 6 to 7 days, after which the crystal phase was rinsed with hot water, air-dried, and subjected to physicochemical analysis (including spectrometry studies on a UR-20 spectrometer, x-ray phase analysis on a URS-50 diffractometer, differential thermal analysis using a PRT-1000M furnace with programmed temperature control, and crystal optics analysis with an MIN-8 polarization microscope. The resultant data were used to plot a

diagram of the crystallization fields of the individual compounds in the system  $Rb_2O$ - $Gd_2O_3$ - $P_2O_5$ - $H_2O$  at 350°C. As in the case of the system Cs-Gd, two gadolinium ultraphosphate structures, i.e.,  $GdP_5O_{14}$ -I and  $GdP_5O_{14}$ -III, formed when the melt's alkalinity was low. The distinction of the formation of the gadolinium ultraphosphate structures in the study compound, however, lay in the fact that the  $GdP_5O_{14}$ -III is generally the main phase in those sections of the system with a minimal content of alkaline component (up to 6-8% by mass), whereas as the domain boundary is approached (i.e., an  $Rb_2O$  content of 16 to 20% by mass), there is a gradual transition to  $GdP_5O_{14}$ -I until it totally replaces the initial structure at the boundary. The binary polyphosphate  $RbGd(PO_3)_4$ -IV was observed to form in a very broad crystallization interval. The cyclotetraphosphate  $RbGdP_4O_{12}$ -A formed along with the latter in a narrow concentration interval. Two additional structures formed when the amount of  $Rb_2O$  in the melt was increased:  $RbGdHP_3O_{10}$  and  $Gd(PO_3)_3$ . The formation of a cubic modification of the binary cyclotetraphosphate  $RbGdP_4O_{12}$ -C was also established. By way of the example of the synthesis of the latter, the researchers succeeded in demonstrating that a cubic phase may be formed by reacting rubidium with rare earth elements (from La to Gd). Figures 2, tables 2; references 8: 7 Russian, 1 Western.

### Thermochemistry of High Temperature Superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$

927M0085A Dushanbe DOKLADY AKADEMII NAUK TADZHIKSKOY SSR in Russian Vol 34, No 2, Feb 91 (manuscript received 7 May 90) pp 102-105

[Article by I. N. Pyagay, O. I. Rakhmatov, and Z. Z. Khasanova, Chemistry Institute imeni V. I. Nikitin; presented by Corresponding Member U. M. Mirsaidov, 27 Apr 90; UDC 541.11]

[Abstract] Selecting the optimum synthesis conditions for high temperature superconductor materials is enhanced with the availability of dependable thermodynamic data. Ceramic materials of this type in particular have not been well studied. In the present work single crystals of the title compound were synthesized and the standard heat of enthalpy determined, viz.  $\Delta H^\circ_{298} = -874.542 \text{ kcal/mole} = -3659.088 \text{ kJ/mole}$ . References 9: 6 Russian, 3 Western.

### The Sorption Properties of Polyamines in Relation to Platinum Metals and Gold

927M0125A Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 37 No 3, Mar 92 (manuscript received 12 Aug 91) pp 649-656

[Article by G.I. Malofeyeva, O.M. Petrukhin, M.V. Akhmanova, P.A. Gembitskiy, N.A. Kleshcheyeva, and T.V. Danilova, Geochemistry and Analytical Chemistry Institute imeni V.I. Vernadskiy, USSR Academy of Sciences, and Petrochemical Synthesis Institute imeni A.V. Topchiyev, USSR Academy of Sciences; UDC 546.91:541.183]

[Abstract] The authors of the study reported herein examined the sorption properties of a number of nitrogen-containing heterochain sorbents based on amines and guanidines of various basicity in relation to platinum metals and gold. Specifically, the researchers examined the effect of the following on the sorption properties of the study polyamine sorbents: basicity of the starting amine, nature of the cross-linking and alkylating reagents, degree of cross-linking, and ratio of secondary and tertiary nitrogen in the sorbent's structural fragment. The study amine-based sorbents were synthesized from branched polyethylene imines with a molecular mass of  $10^4$  that contained 25-30% primary, 25-30% tertiary, and 40-50% secondary nitrogen and from diethylenetriamine. The ratio of secondary and tertiary nitrogen in the polyamines was varied depending on the conditions of the reactions involving the cross-linking and alkylating reagents. The polyethylene imines were structured into a three-dimensional gel by reacting them with 1,6-dichlorohexane, 1,3-dichloropropene, and 1,2-dibromoethane. The degree of cross-linking was varied by involving between 10 and 80% amine groupings of the starting polyimine in the reaction. The studies performed established that changing the ratio of tertiary

to secondary nitrogen in polyethylene imine-based sorbents from 0.6 to 40 in the pH interval from 5 to 1 does not result in any change in sorption properties in relation to iridium and palladium. Sorption of iridium from a solution in the pH interval from 5 to 1 remained at the 88% level, and sorption of palladium remained at the 97% level. In a solution of 1 M HCl, the amount of palladium extracted dropped to 63% on average, whereas sorption of platinum and gold under the same conditions remained at the 95% level. Thirty minutes was required to reach maximum extraction. Differences in sorption behavior did appear in more acidic media, however. As the content of tertiary nitrogen in the sorbent was increased, the maximum degree of iridium extraction was maintained over a broader interval of change in acidity; for example, the degree of iridium extraction by a sorbent with a tertiary-to-secondary nitrogen ratio of 40 in 3 and 6 M HCl amounted to 84 and 82%, respectively, whereas the degree of extraction by a sorbent with a tertiary-to-secondary nitrogen ratio of 0.6 amounted to 71 and 63% respectively in the aforesaid solutions. Increasing the sorption time in such cases did not change the extent of extraction. Increasing the relative percentage of tertiary nitrogen atoms in the sorbent, on the other hand, made it possible to maintain higher degrees of iridium and palladium extraction over a somewhat broader range of change in pH. The sorbents studied proved to be rather selective. The presence of alkaline, alkaline earth elements, a series of nonferrous metals, and iron did not reduce the completeness of extraction of platinum metals. Using a starting amine with a somewhat lesser basicity and more ordered structure did not alter the sorption properties of the gels studied. The sorbents based on polyhexamethylene-guanidine and 1,6-di(biguaniidohexane) were much less effective than were polyethylene imine sorbents with respect to the sorption of iridium and palladium. Polyethylene imine polymers with a high nitrogen content (12 to 15%) thus proved to be rather effective sorbents for concentrating platinum metals and gold. The studies also indicated that there is a threshold point beyond which increasing the basicity of the amine will have a negative effect. Figures 3, tables 2; references 15: 14 Russian, 1 Western.

### Data Bank on the Properties of Ternary Inorganic Compounds as the Basis for the Computer-Aided Design of New Substances

927M0125B Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 37 No 3, Mar 92 (manuscript received 22 Jul 91) pp 698-702

[Article by N.N. Kiseleva and N.V. Kravchenko, Metallurgy Institute imeni A.A. Baykov, USSR Academy of Sciences; UDC 681.31:546.0:548.30]

[Abstract] The Faza data bank, which was created at the Metallurgy Institute imeni A.A. Baykov of the USSR Academy of Sciences, contains information on the properties of ternary inorganic compounds. The Faza data bank is a component of a data bank on the properties of inorganic phases that is being developed. The Faza data bank was developed on the basis of the BOYaZ-6 data

base programming system (for use with BESM-6 computers). The data bank is currently being converted for use on the IBM PS/2 (with the rBase DBMS). The data bank contains information on the thermochemical, crystal chemistry, superconductive, acoustooptical, electrooptical, and nonlinear optics properties of about 35,000 known ternary compounds as drawn from 9,000 bibliographic sources. The following information is provided about each compound: quantitative and qualitative composition of the compound; type of melting (at 1 atm); melting point (at 1 atm); boiling point (at 1 atm); decomposition temperature in both the solid and gaseous phase (at 1 atm); and types of crystalline structures. The following additional information is provided under the latter information category: temperature and pressure at which the said crystal modifications are formed; syngony; Fedorov group; number of formula units in an elementary cell; critical temperature of transition to a superconductive state; upper critical magnetic field at 4.2 K; refractivity as a function of radiation wavelength; coefficients of thermal expansion as a function of temperature; heat conductivity as a function of temperature; dielectric constants as a function of frequency of the applied electric field; electrooptic coefficients as a function of radiation wavelength; nonlinear optical coefficients as a function of radiation wavelength; dielectric losses; transmission range; angle of synchronism; water solubility at room temperature; heat capacity as a function of temperature; piezoelectric coefficients; elastic constants, elasto-optical coefficients as a function of radiation wavelength; rate of elastic wave propagation as a function of the direction and type (lengthwise or crosswise) of elastic wave; coefficients of an elastic wave's attenuation factor in a crystal at a fixed frequency as a function of the direction of propagation and the type of elastic wave propagated; crystal lattice parameters; density; and Curie point. The Faza data bank is intended for inorganic chemists, materials specialists, and engineers. All users of the USSR Academy of Sciences Computer Center have interactive access to the Faza data bank. The Faza data bank may be used in conjunction with an artificial intelligence system to forecast new inorganic phases and to estimate their properties. The Faza data bank's knowledge base will store those laws that have already been discovered to govern different classes of inorganic compounds. Information included in the knowledge base will be represented in terms of a semantic net. An interactive process helps users who are not trained computer users to work with the forecasting information system. References 14: 12 Russian, 2 Western.

#### Investigation of Anisotropy of the Surface Energy of Cadmium Diarsenide Monocrystals

927M0126A Moscow ZHURNAL  
NEORGANICHESKOY KHIMII in Russian Vol 37  
No 4, Apr 92 (manuscript received 12 Aug 91)  
pp 719-723

[Article by V.P. Sanygin, A.M. Raukhman, and V.B. Lazarev, General and Inorganic Chemistry Institute imeni N.S. Kurnakov, Russian Academy of Sciences; UDC 548.3+536.654]

[Abstract] The authors of the study reported herein examined the problem of anisotropy of the surface energy of cadmium diarsenide monocrystals. First, the researchers calculated the anisotropy of the surface energy of the II-V compound cadmium diarsenide based on data from a calculation of the enthalpy of the chemical bonds Cd-As and As-As bonds. Next, they checked the accuracy of the said results by taking microhardness measurements on planes parallel to crystallographic planes of type (001), (100), and (110) monocrystals grown by the method of resublimation and by the Bridgman method. A PMT-3 hardness tester was used to measure the specimens' microhardness, and a DRON-3 x-ray diffractometer was used to identify the faces of those crystals that were produced from a vapor phase and to orient (with a precision of 0.5°) those monocrystals that were produced from a melt. The calculations based on crystal chemistry data were found to be in good agreement with data from a study of the microhardness of CdAs<sub>2</sub> monocrystals grown from both a vapor phase and a melt. In view of the discrepancy between the overall parameters of the crystal chemistry model of cadmium diarsenide and its generally accepted structural parameters, however, the researchers recommended increasing the parameters of the elementary cell of the study semiconductor compound to the dimensions of its crystal chemistry model. The recommended changes were as follows:  $a' = a \times \sqrt{2} = 1.1247$  and  $c' = 3c = 1.4025$  nm (versus the generally accepted values of  $a = 0.7953$  and  $c = 0.4675$ ). On the basis of their analysis, the researchers concluded that the anisotropy of the microhardness of perfect, practically dislocation-free cadmium diarsenide monocrystals fits within the scheme of the anisotropy of specific surface energy obtained by calculations based on data from a crystal chemistry analysis of the said semiconductor compound. Figures 3, tables 3; references 6: 5 Russian, 1 Western.

#### The Extraction of Silver From Halide and Rhodanate (Thiocyanate) Solutions by Antipyrine Derivatives in a Mixture of Organic Solvents

927M0126B Moscow ZHURNAL  
NEORGANICHESKOY KHIMII in Russian Vol 37  
No 4, Apr 92 (manuscript received 14 Mar 91)  
pp 954-957

[Article by V.O. Kordyukovich, V.L. Giruts, and V.I. Kuznetsov, Moscow State University imeni M.V. Lomonosov and Nuclear Physics Scientific Research Institute; UDC 546.57:542.61]

[Abstract] The technique of using a mixture of active organic solvents to extract silver from halide and thiocyanate solutions is interesting in that it results in a synergistic effect (more complete extraction is achieved by using a mixture of solvents than by the individual use of any of the solvents in a given mixture). When solvent mixtures are used, the active solvent is diluted by the inert solvents. A few active solvents, however, are capable of self-association, and their effective concentrations increase upon dilution. In view of these facts, the

authors of the study reported herein studied the extraction of silver at concentrations of  $10^{-4}$  to  $10^{-6}$  mol/l from acidic chloride, bromide, iodide, and thiocyanate solutions by antipyrene derivatives in a mixture of active ( $\text{CHCl}_3$  and  $\text{C}_2\text{H}_4\text{Cl}_2$ ) and inert ( $\text{CCl}_4$ ,  $\text{C}_2\text{Cl}_4$ ,  $\text{C}_7\text{H}_{16}$ , and kerosene) solvents. The limiting dilution of the active solvent by the inert solvent was determined by the formation of a sediment of acidic salt of the reagent. The reagents were synthesized in accordance with a method described elsewhere, and  $\text{H}_2\text{SO}_4$  was used to create the required acidity. The element content in the phases was determined radiometrically by using  $^{110m}\text{Ag}$ . A phase contact time of 1 hour was used, and complete stratification of the phases was accomplished by centrifugation. The experiments performed established that the ionic associate of silver solvated by the respective acidic salt of the reagent and the active organic solvent is extracted into the organic phase. The process of solvation of the ionic associate by the reagent salt proved to be prevailing in the iodide and thiocyanate systems, thus reducing the coefficient of distribution as the concentration of active solvent in the mixture is increased. In the chloride system, on the other hand, solvation of the ionic associate by the active organic solvent proved to be the factor that determines the completeness of extraction. The bromide system was found to occupy an intermediate position between the two aforesaid types of systems. The studies further indicated that the interconnection between the processes at work during the solvation of the extracted ionic associate restricts the applicability of the log-log method of determining the solvate number in a hydrate-solvate mechanism of extraction in the systems studied. Figures 3, tables 4; references 6 (Russian).

### Reaction in Mixtures of Aluminum Oxide and Potassium and Sodium Bifluorides

927M0127C Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 37 No 5, May 92 (manuscript received 10 Oct 91) pp 1015-1018

[Article by B.F. Dmitruk, N.N. Yashchenko, O.G. Zarubitskiy, and G.N. Novitskaya, Ukraine General and Inorganic Chemistry Institute; UDC 546.04:54.386]

[Abstract] The authors of the study reported herein used the methods of comprehensive thermal analysis and x-ray phase analysis to investigate the reactions occurring in the binary and ternary mixtures  $\text{MHF}_2\text{-Al}_2\text{O}_3$  ( $M = \text{K}, \text{Na}$ ) and  $\text{KHF}_2\text{-NaHF}_2\text{-Al}_2\text{O}_3$  given a 6:1 molar ratio of the salt or salt mixture to the oxide. Analytically pure  $\alpha\text{-Al}_2\text{O}_3$  and potassium and sodium bifluorides were subjected to additional purification by recrystallization and drying before being used in the study. The studies were performed on a Q-1500D derivative differential thermal analyzer. The study specimens were heated in air in open platinum crucibles at a rate of  $10^\circ/\text{min}$ . Weighted portions of starting material in the amount of 1.3 to 1.8 g were studied. In the mixture

$6\text{KHF}_2\text{-Al}_2\text{O}_3$ , the reaction began at  $200^\circ\text{C}$ . It was exothermal and occurred very intensely, peaking after several minutes. The temperature of the onset of the reaction did not change significantly when the heating rate was reduced from 10 to  $5^\circ/\text{min}$ . Analysis of the reaction product established that potassium hexafluoroaluminate evidently forms in a single stage. The mixture  $6\text{NaHF}_2\text{-Al}_2\text{O}_3$  behaved differently: Sodium fluoride and aluminum oxide were detected in it after it had been heated to  $400^\circ\text{C}$ . Salt decomposition was thus determined to be the main process at work in mixtures of sodium bifluoride and aluminum oxide. The reactions occurring in the system  $\text{KHF}_2\text{-NaHF}_2\text{-Al}_2\text{O}_3$  were investigated with the system components in molar ratios of 3:3:1 and 4:2:1. The analyses performed confirmed the researchers' hypotheses that the formation of potassium-sodium hexafluoroaluminate and the decomposition of excess  $\text{NaHF}_2$  would result from the reaction of an equimolar ratio of salts in a ternary mixture. The said reaction began at about  $160^\circ\text{C}$ .  $\text{K}_2\text{NaAlF}_6$  was the main product of the reaction of the 4:2:1 mixture; a far smaller amount of sodium fluoride was also established. It was further confirmed that practically pure  $\text{K}_2\text{NaAlF}_6$  may be obtained from  $4\text{KHF}_2\text{-}2\text{NaHF}_2\text{-Al}_2\text{O}_3$  at a temperature of 180 to  $200^\circ\text{C}$ . The nature of the cation was found to largely dictate product composition and reaction kinetics in the system studied. During the course of their investigation, the researchers also refined the parameters of the crystal lattice of potassium bifluoride. Specifically, they established the following as the parameters of a tetragonal elementary cell of  $\text{KHF}_2$  (in angstroms):  $a = 5.648 \pm 0.004$  and  $c = 6.810 \pm 0.004$ , with the number of formula units amounting to  $Z = 4$ . The density of potassium fluoride as determined in toluene was found to equal  $2.38 \pm 0.005 \text{ g/cm}^3$ , which is in good agreement with the calculated density of  $2.40 \text{ g/cm}^3$ . Figure 1, tables 2; references 7: 5 Russian, 2 Western.

### Effect of Solvent, Electrolyte, and Surfactant on the Electrode Behavior of Ion-Selective Field-Effect Transistors With Silicon (IV) Oxide and Tantalum Oxide (V) Films

927M0130D St. Petersburg ZHURNAL PRIKLADNOY KHIMII in Russian Vol 64 No 12, Dec 91 (manuscript received 9 Aug 91) pp 2619-2629

[Article by P.V. Bobrov, A.V. Bratov, and Yu.A. Tarantov, St. Petersburg State University; UDC 541.135.5]

[Abstract] In an effort to clarify the laws governing the pH sensitivity of ion-selective field-effect transistors with oxide films and to determine whether they may be described based on the theory of surface bound states, the authors of the study reported herein analyzed the effect that electrolyte and solvent nature and surfactant adsorption have on the electrode behavior of the said transistors. The researchers also made a comparative study of the electrode properties of ion-selective field-effect transistors with  $\text{SiO}_2$  and  $\text{Ta}_2\text{O}_5$  films in aqueous

solutions containing different types of surfactants, anhydrous solutions, and mixed solutions. Special attention was paid to the effect of the cations of the background electrolyte. The effects that the solvent, surfactant, and background electrolyte have on the electrode behavior of ion-selective field-effect transistors with oxide films turned out to be predictable from a model of surface bound states. Surfactant type and size of the cations of the background electrolyte were found to have a strong effect on the behavior of ion-selective field-effect transistors with an  $\text{SiO}_2$  film that was also explainable within the framework of a model of surface-bound states. Specifically, adding ionogenic surfactants to the solution was found to significantly distort their V-pH curves, with the strongest effects being observed in the acidic region and depending on the type of surfactant (adding cetyltrimethyl ammonium bromide resulted in an increase in V, whereas adding sodium dodecylsulfate resulted in the opposite effect). The researchers encountered problems when they attempted to explain the electrode properties of ion-selective field-effect transistors with a  $\text{Ta}_2\text{O}_5$  film based on a model of surface bound states. The electrode behavior of ion-selective field-effect transistors with a  $\text{Ta}_2\text{O}_5$  film in anhydrous solutions was found to be characterized by the following: the absence of any specific effect of the solvent; a broad range of ideal pH sensitivity; and alkaline errors that increased in the order K - Na - Li. The researchers hypothesized that one possible reason for these problems is that a layer that is penetrable by alkaline metal protons and cations and that is analogous to the ion-exchange layer of a glass electrode exists on the surface of  $\text{Ta}_2\text{O}_5$ . Figures 4, tables 2; references 15: 10 Russian, 5 Western.

#### The Nonmagnetic Mechanism of Kinetic Isotope Effects in Reactions of the Photochemical Reduction of Uranyl

927M0132A Moscow KHIMICHESKAYA FIZIKA  
in Vol 11 No 1, Jan 92 (manuscript received  
12 Mar 91) pp 54-68

[Article by V.S. Mironov and S.P. Rozov, Physical Chemistry Institute, USSR Academy of Sciences, Moscow; UDC 541.14:546.791]

[Abstract] The authors of the study reported herein examined the distinctive features of the elementary acts of electron transfer within the radical pair  $[\text{UO}_2^+, \text{RH}]$  that are associated with the specifics of the electron structure of the 5f shell of uranium (a strong spin-orbital interaction in conjunction with the unfrozen orbital moment of the 5f electron and the spatial anisotropy of the 5f orbitals). Special attention was paid to four problems: the electron structure of the excited uranyl ( $\text{UO}_2^{2+}$ ) and its connection with the spin state of the radical pair  $[\text{UO}_2^+, \text{RH}]$ ; the electron structure of the 5f shell in the reduction products of  $\text{UO}_2^{2+}$ , i.e.,  $\text{UO}_2^+$  and  $\text{U}^{4+}$ ; the effect that the anisotropy of the 5f orbitals and nature of the distribution of spin density in  $\text{RH}$  radicals has on the likelihood of electron transfer within the

radical pair  $[\text{UO}_2^+, \text{RH}]$ ; and the role of spin prohibitions in processes of intracellular reduction and oxidation of  $\text{UO}_2^+$  in the radical pair  $[\text{UO}_2^+, \text{RH}]$  in light of the specifics of the electron structure of  $(\text{UO}_2^+)^*$ ,  $\text{UO}_2^+$ ,  $\text{U}^{4+}$ . On the basis of published experimental and theoretical data, the authors proceeded to propose a new nonmagnetic mechanism of the isotope effects occurring in the radical pair  $[\text{UO}_2^+, \text{RH}]$ . The proposed mechanism is based on the orbital prohibition against electron transfer between  $\text{UO}_2^+$  and the organic radical for the first excited electron state  $[\text{g} < \text{j} \neq 3/2]$  of the ion  $\text{UO}_2^+$  and the different lifetimes of this state for the isotopes  $^{235}\text{U}$  and  $^{238}\text{U}$ . The proposed nonmagnetic mechanism makes it possible to explain both the signs and orders of magnitude of the isotope effects occurring in the systems  $\text{UO}_2^{2+}$ -p-methoxyphenol and  $\text{UO}_2^{2+}$ - $\text{C}_2\text{O}_4^{2-}$ . Figures 6, table 1; references 18: 10 Russian, 8 Western.

#### Acceleration of Low-Temperature Chemical Reactions in Hydrocarbon Glass by Acoustic Waves. 1. Molecular Mobility Activated by Mechanical Loading

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in Vol 11 No 1, Jan 92 (manuscript received  
28 Feb 91) pp 103-109

[Article by P.G. Filippov and V.M. Beskrovnyy, Energy Problems of Chemical Physics Institute, USSR Academy of Sciences, Moscow; UDC 541.141.1]

[Abstract] The authors of the study reported herein used the methods of pulse strain measurement and dielectric spectroscopy to examine the time dependence of the relative deformation  $\Delta$  and change in the angle of tangence of dielectric losses  $\text{tg } \delta_e$  of vitreous solutions of chlorine in methylcyclopentane subjected to pulsed unilateral mechanical loading during the course of an explosive chlorination reaction in the end face of the specimen. The study specimens had a  $\text{Cl}_2$ -to-hydrocarbon molecular molar ratio of 1:2.5. The pulsed loading was created by using a nitrogen laser with a wavelength of 337 nm to create a radical concentration of about  $10^{19} \text{ cm}^{-3}$ . After photolysis, the specimens were cooled at a rate of about  $0.1 \text{ k} \times \text{s}^{-1}$  to a temperature of about 40 K. Rapid heating at 150-200 K and expansion of the matter as a result of the intensive release of the liquid and gas products of the reaction in the end face then created a pulse that created a load throughout the bulk of the specimens. The relative internal deformations  $\Delta$  along the long axis of the specimens were measured by a wire strain gauge measuring  $0.1 \times 0.2 \times 0.05 \text{ cm}$  that had been frozen into the glass. A bridge measuring circuit was used. The dielectric characteristics of the mixtures were measured at a frequency of  $10^4 \text{ Hz}$  by using an R-4058 alternating-current bridge. The kinetics of the change in  $\text{tg } \delta_e$  during pulsed loading were measured by the capacitive method based on the change in  $\epsilon$  of the mixture. The studies performed established that at a temperature of 40 K, a pulsed compression rate of about  $1 \text{ s}^{-1}$ , and a pulsed compression amplitude of  $2 \text{ to } 3 \times 10^{-3}$ ,  $\text{tg } \delta_e$  increases to values characteristic of the devitrification

region. The observed increase in  $\tan \delta_a$  was not determined to be related to local heating of the glass but was instead found to be caused by an increase in molecular mobility during the "cold" glass flow. Figures 2; references 25: 20 Russian, 5 Western.

**Quantum Chemical Computations of Parameters of Single-Electron Band Structure of Sulfur- and Selenium-Containing Organic Superconductors. 1. Theoretical Model**

927M0134A Moscow KHIMICHESKAYA FIZIKA  
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11 May 91) pp 307-314

[Article by A.A. Guliyev, I.A. Abronin, and V.P. Litvinov, Theoretical Problems of Chemical Technology Institute, Republic of Azerbaijan Academy of Sciences and Organic Chemistry Institute, Russian Academy of Sciences, Moscow; UDC 530.145:543.422:539.194.541.49]

[Abstract] In this first of a two-part study, the method of LCAO-MO-SCF [self-consistent field theory of molecular orbitals in a linear combination of atomic orbitals] in a CNDO [complete neglect of digital overlap] valence approximation has been used to calculate the parameters of five different dimer forms of tetramethyltetraselenofulvalene ( $TMTSF_2$ ). First, the parameters of the single electron band structure of the neutral system were calculated. Calculations were also performed with consideration for charge transfer based on a theoretical model that was developed in an approximation of a strong bond. The calculations were performed on an *sp* basis on a YeS-1060 computer. The widths of the forbidden zone inside the chain, i.e.,  $W(a)$ , and the forbidden zone in a crosswise direction, i.e.,  $W(b)$ , were calculated for various amounts of charge transfer. The following values were calculated for the neutral system  $(TMTSF_2)PF_6$ :  $W(a) = 2.88$  eV and  $W(b) = 98$  meV. According to a communication published elsewhere, computation by the method of displacement of the plasma edge results in values of  $W(a) = 1.2$  eV and  $W(b) = 13$  meV. According to yet another source that reflects a more painstaking analysis,  $W(b) = 140$  meV. The analysis and calculations reported herein confirm the findings of another publication demonstrating that each  $TMTSF$  molecule participates in the formation of  $(TMTSF_2)X$  ( $X = PF_6^-$ ,  $AsF_6^-$ ,  $ClO_4^-$ , etc.) with an identical valence of 0.5 in the case of  $(TMTSF)_2^+X^-$ . Analysis of the data regarding effective charges on atoms in the dimer  $(TMTSF)_2$  and the neutral molecule  $TMTSF$  demonstrates that the charge is primarily transferred from the selenium atom and that the relative contribution to the total sum of charge transfers from these selenium atoms remains unchanged for different extents of charge transfer. These facts led the authors to conclude that using semiempirical methods of the self-consistent field theory of molecular orbitals in a linear combination of atomic orbitals together with spectroscopic parametrization within the framework of their proposed theoretical model in an approximation of a strong bond makes it possible to obtain reasonable

estimates for the characteristics of the simple single-electron band structure of both a neutral system and complexes in which charge transfer occurs. Figures 3, tables 3; references 17: 5 Russian, 12 Western.

**Quantum Chemical Computations of Parameters of Single-Electron Band Structure of Sulfur- and Selenium-Containing Organic Superconductors. 1. The Effect of Chemical Nature and Structure of the Donor Component**

927M0134B Moscow KHIMICHESKAYA FIZIKA  
in Vol 11 No 3, Mar 92 (manuscript received  
11 May 91) pp 315-321

[Article by A.A. Guliyev, I.A. Abronin, and V.P. Litvinov, Theoretical Problems of Chemical Technology Institute, Republic of Azerbaijan Academy of Sciences and Organic Chemistry Institute, Russian Academy of Sciences, Moscow; UDC 530.145:543.422:539.194.541.49]

[Abstract] In this second of a two-part study, the method of LCAO-MO-SCF [self-consistent field theory of molecular orbitals in a linear combination of atomic orbitals] in a CNDO (complete neglect of digital overlap) valence approximation has been used to calculate the parameters of the band structure of selected heterofulvalenes containing sulfur and selenium atoms. The authors' primary objective in conducting this study was to predict the most promising organic donors for producing complexes with charge-transfer complexes with specified properties, specifically with the highest temperature of transition into a state of superconductivity [ $T_c$ ]. The researchers began their efforts to construct the crystal fragment of a charge-transfer complex based on the proposed heterofulvalenes I-III with data in published roentgenographic studies of the structure of  $(TMTTF)_2X$ ,  $(TMTSF)_2X$ ,  $(BEDT-TTF)_2X$ , and other related compounds. The computations were performed in two stages. First, neutral complexes were calculated in order to determine the most promising donor relative to interchain interaction. Next, the dependence between the degree of charge transfer and the electron structure of the study heterofulvalene was determined. The calculations performed established that heterofulvalenes containing heteroatoms of different natures with a trans-structure are characterized by the presence of relatively strong interchange molecular interaction. This interaction in turn was found to result in a significant increase in the degree of two-dimensionality of the conduction of charge-transfer complexes based on them. The nature of the change in electron structure of the study donors as a function of degree of ionization was examined. Data presented regarding the band structure of the isomer II(b), for example, revealed that as charge transfer increases, intermolecular interaction within the chain is attenuated slightly, and the corresponding width of the band  $W(a)$  decreases from 2.2 eV for neutral II(b) to 2.0 eV at the maximum value of  $Q = 1.0e$ . A slight increase in  $Q$  from 0.4e to 0.5e, on the other hand, results in a significant increase in the crosswise width of the band

W(b) due to an increase in interchain molecular interaction. For the heterofulvalene II(b) and  $(\text{TMTSF})_2\text{PF}_6$ , the researchers obtained  $T_c$  values of 90 and 18 K, respectively. From this standpoint, heterofulvalenes were deemed extremely promising compounds whose calculated  $T_c$  values are severalfold higher than those calculated for known  $(\text{TMTSF})_2\text{X}$  crystals. Figures 2, tables 3; references 11: 7 Russian, 4 Western.

### The Quantum Yield of Photogeneration of Carriers in Materials With Anisotropic Conduction

927M0134C Moscow KHIMICHESKAYA FIZIKA  
in Vol 11 No 3, Mar 92 (manuscript received  
21 May 91) pp 336-343

[Article by V.I. Arkhipov and V.R. Nikitenko, Moscow Physics Engineering Institute; UDC 537.31:541.64]

[Abstract] The authors of the study reported herein conducted a theoretical analysis of heminal recombination in materials with anisotropic mobility, anisotropic diffusivity, and dielectric permittivity. The analysis was based on a model that was in turn based on Smolukhovskiy's equation for an anisotropic medium. In an approximation of prescribed diffusion, the authors derived an analytical solution of the said equation for an arbitrary degree of anisotropy of the material, intensity of the electric field, and initial distribution of the twins in pairs. Two initial distributions were analyzed. The first was the spherically symmetrical function that arises in the case of generation by nonpolarized radiation and under conditions where the hot carriers are insensitive to the anisotropy of the mobility of the thermalized carriers. The second was the "ellipsoidal" initial distribution that occurs in the case of generation by unpolarized light provided that the hot carriers have the very same anisotropy of mobility that occurs in the case of thermalized carriers. This solution was then used to analyze the temperature and field dependences of the quantum yield of photogeneration of carriers for materials with different degrees of anisotropy. The analysis established that quantum-yield activation energy increases sharply as the degree of anisotropy increases. This proved to be especially true in cases of ellipsoidal initial generation. The theoretical results obtained during the course of the analysis reported were found to be in good agreement with numerical and experimentally obtained data present in the literature. The authors concluded their analysis by stating that experiments usually reveal the that recombination and/or charge carriers in the volume outside the Onsager radius have a significant effect on the quantum yield of free carriers and that in cases of a high degree of anisotropy, the likelihood of heminal recombination begins to depend on diffusion length (to the center of recombination in the bulk) even though it is much larger than the Onsager radius. In light of this fact, the authors acknowledged that a term corresponding to the drain to the recombination centers might be included in their initial equation. This would in turn result in a

significant increase in quantum yield in cases of small electric fields. Figures 3; table 1; references 11: 1 Russian, 10 Western.

### Tunneling of Two Interacting Particles Moving Parallel or Antiparallel

927M0135C Moscow KHIMICHESKAYA FIZIKA  
in Vol 11 No 5, May 92 pp 738-746

[Article by Yu.I. Dakhnovskiy and M.B. Semenov, Chemical Physics Institute imeni N.N. Semenov, Russian Academy of Sciences, Moscow; UDC 539.192]

[Abstract] The authors of the study reported herein examined the tunneling of two interacting particles moving in parallel or antiparallel directions. Specifically, they studied the dependence of the tunneling rate constants on temperature and strength of the bond between the particles. Two physically different transfer situations were considered. In the first scenario considered, it was assumed that the particles are moving in parallel. In the second scenario, it was assumed that the particles are moving in opposite directions (antiparallel). The general formalism of the instanton approach to the problem of quantum tunneling with dissipation was used. This made it possible to also consider interaction with oscillators in the surrounding medium (a thermostat). The calculations performed revealed that in the case where tunneling particles are moving along parallel reaction coordinates in a single direction (parallel) in an asymmetrical adiabatic potential, two sub-barrier trajectories close to the main tunnel trajectory ( $R_1 = R_2$ ) will split off from it at some temperature  $T_c$ . This critical temperature was found to be a function of the coefficient of interaction between the particles. Similar "splitting off" was demonstrated to be disadvantageous from an energy standpoint for cases of antiparallel tunnel transfer of particles; instead, movement along a single two-dimensional trajectory (synchronous transfer) was found to be most advantageous in cases of antiparallel transfer. In cases of both parallel and antiparallel tunneling, giving consideration to interaction with the surrounding medium did not have any qualitative effect on the nature of the transfer. From a quantitative standpoint, on the other hand, interaction with the surrounding medium did have different effects on antiparallel and parallel particle transfer. The analysis established that the surrounding medium always has an effect on the parallel motion of tunneling particles but does not affect the magnitude of the effect along the main trajectory in cases of antiparallel motion of tunneling particles. Figures 4; references 32: 6 Russian, 26 Western.

### Effect of Disperion Medium on Rheological Properties of Dispersed Extended Graphite

927M0148D Moscow KOLLOIDNYY ZHURNAL  
in Russian Vol 54, No 2, Mar-Apr 92 (manuscript  
received 9 Aug 89) pp 133- 138

[Article by S. V. Pakhovchishin, A. A. Chuyko, I. G. Chernysh, and V. F. Gritsenko, Surface Chemistry Institute, Kiev; UDC 541.180]

[Abstract] Optimization of the properties of graphite-based composite materials requires study of both the surface properties of the dispersed particles and the various aspects of interactions between the dispersed phase and the dispersion medium. Recently published work on the rheological properties of dispersed graphite in various media revealed the important role played by non-hydrodynamic parameters. The rheological properties of dispersions of the various forms of graphite have not yet been investigated. In the

present work a study of the structural and mechanical properties of dispersed extended graphite in both polar and non-polar media demonstrated that effective viscosity is directly proportion to the dielectric constant of the dispersion medium. The role of the morphological features of extended graphite particles resulting from its method of preparation, normally difficult to evaluate, becomes more significant as conditions become static. Figures 2; references 9: 8 Russian, 1 Western.

**Organometallic Biochemistry: Regeneration of Nicotineamide Cofactors in Presence of Pentamethylcyclopentadienyl Complexes of Rhodium**

927M0138A Moscow METALLO-ORGANICHESKAYA KHIMIYA in Russian Vol 5, No 1, Jan-Feb 92  
(manuscript received 1 Apr 91) pp 162-170

[Article by A. D. Ryabov and D. L. Menglet, National Economy Institute, Moscow; Moscow State University imeni M. V. Lomonosov; UDC 577.15]

[Abstract] Organometallic biochemistry is a modern outgrowth of biochemistry and enzymology on the one hand, and organometallic chemistry on the other. Its vigorous development is enhanced chiefly by the increase in content of organometallic compounds in the environment resulting from the greater use of these compounds in industry. Organometallic molecules engage in various biochemical and microbiological reactions, and the task facing modern scientists is the development of ways to combine enzymes and organometallic molecules into a single complex. The final goal of the present work is the development of a system of regeneration of cofactors and biosensor devices. A study was therefore made of the electrochemical mechanism of the intermolecular reduction of nicotineamideadeninedinucleotide (NAD<sup>+</sup>) with rhodium complexes. Rhodium (III) complexes with adenine were synthesized by oxidation of NAD<sup>+</sup>). It was demonstrated that the new complexes are electrochemically active and that the complex with modified cofactor enters catalyzed formate and alcohol dehydrogenase enzymatic processes. The adenine ring may serve as a donor site for metal-mediator ions in electron transport without loss of enzymatic activity. The rhodium (III) complex oxidizes NADH to NAD<sup>+</sup> and is reduced to rhodium (I). Since rhodium (I) can be electrochemically oxidized to rhodium (III), a new possibility opens up for developing cofactor regeneration based on pentamethylcyclopentadienyl rhodium. Figures 7; references 15: 2 Russian, 13 Western.

**Sandwiched, Semi-Sandwiched, and Multi-Decked Clusters**

927M0138B Moscow METALLO-ORGANICHESKAYA KHIMIYA in Russian Vol 5, No 1, Jan-Feb 92  
(manuscript received 1 Apr 91) pp 194-212

[Article by A. R. Kudinov, D. V. Muratov, and M. I. Rybinskaya, Elementoorganic Compounds Institute, Moscow; UDC 541.49:542.91:546.96:547.1'13]

[Abstract] It was previously demonstrated that  $\pi$ -complexes of transition metals may also be described as clusters from the standpoint of the theory of polyhedral skeletal electron pairs, and the concepts developed in these works have been widely used in inorganic and coordinate chemistry. However, an opposite view, of great interest to metalloorganic chemists, namely the correlation of metal-containing groups in clusters with organic ligands, has not yet been sufficiently clarified. In

the present work an attempt was made to correlate three-member metallo-cyclics, consisting entirely of metal atoms, with hydrocarbon cyclic ligands. These concepts were formulated on the basis of experimental data and an analysis of published data. It was demonstrated that the tri-rhodium metallo-cyclic  $Rh_3(C_5H_5)_3(\mu-CO)_3$  behaves as a 2-electron ligand in respect to the cationic group  $[PPh_3M]^+$ , where M=Cu, Ag, Au), and as a 6-electron ligand in respect to  $[C_5R_3M]^+$ , where M=Fe, R=H; M=Ru, R=H or Me. The data were systematized by sandwich, semi-sandwich, and multi-decked clusters, and it was demonstrated that in the case of three-member metallo-cyclics formed from metals within transition series, there is tendency for 6-electron valency encirclement. Figures 7; references 95: 8 Russian, 87 Western.

**Rearrangement of Complexes of Phosphoryl Compounds With Triethylaluminum**

927M0138C Moscow METALLO-ORGANICHESKAYA KHIMIYA in Russian Vol 5, No 1, Jan-Feb 92  
(manuscript received 16 Jul 91) pp 233-234

[Article by I. A. Trofimtsova, Ye. V. Chechegoyeva, V. V. Gavrilenko, L. A. Chekulayeva, and E. Ye. Nifantev, Moscow Pedagogical State University imeni V. I. Lenin; UDC 547.26:118.07/0.88.8/]

[Abstract] Triethylaluminum complexes of hydrophosphoryl compounds such as phosphonous acids and dialkyl phosphites are shown to be capable of rearrangement with the exchange of alkyl radicals at the aluminum atom with hydrogen at the phosphorus atom. The rearrangement was confirmed with NMR spectra. References 3: 1 Russian, 2 Western.

**Structural Characteristics of Rare Earth Organic Compounds With Metal-Organic Ligands**

927M0139A Moscow METALLO-ORGANICHESKAYA KHIMIYA in Russian Vol 5 No 2, Mar-Apr 92  
(manuscript received 1 Apr 91) pp 279-296

[Article by L. N. Zakharov, Institute of Metal-Organic Chemistry, USSR Academy of Sciences, Nizhniy Novgorod; UDC (546.63-546.66):547.1'13:548.737]

[Abstract] This is a relatively new area of organic chemistry, the first papers dating back to the mid-1970's. A review of x-ray structural studies was presented analyzing the crystalline structures of these rare earth organic compounds containing non-transition elements Si, Ge and Sn. These structures may be ionic, they may exhibit a direct bond Ln-E (Ln = a lanthanoid; E= Si, Ge, Sn) and a Ln-E bond formed with a hydrogen bridge - a tricentric-two-electrons bond. Examples of these three situations were presented with detailed discussion of their geometry, bond length and bond angles. The second part of the review covered an analysis of the effect of non-valent interactions between the ligands on the structure of organic rare earth compounds. The examples

presented illustrated the effect of the degree of shielding of the active centers in these molecules on the structure of condensed states of the lanthanoid compounds, and the applicability of the calculations to analysis of possible occurrence of intermolecular reactions inside their structures. Table 1; figures 15; references 45: 14 Russian, 31 Western (4 by Russian authors).

**Synthesis of Optically Active (2-Methylenenorbornadienyl)rhodiumcyclopentadienyl Cation**

927M0139B Moscow METALLO-ORGANICHESKAYA KHIMIYA in Russian Vol 5 No 2, Mar-Apr 92 (manuscript received 6 Aug 91) pp 474-475

[Article by I. T. Chizhevskiy, Institute of Metal-Organic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow; UDC 547.1'13:546.97]

[Abstract] Synthesis of the first enantiomeric allylolefine complex (+)-[( $\eta^2,\eta^3$ -C<sub>7</sub>H<sub>7</sub>-2-CH<sub>2</sub>)Ph( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)]<sup>+</sup>PF<sub>6</sub><sup>-</sup>, based on previously described split of a racemic (2-acylnorbornadienyl)rhodiumcyclopentadienyl complexes, was reported. Considering the "rigid" structure of the hydrocarbon skeleton of norbornadiene derivatives and relatively soft reaction conditions which exclude the possibility of a split along the norbornadiene ligand-functional group bond, it is reasonable to assume that configuration inversion did not occur in the final

cation product. Based on its cationic structure, this product may be of interest in asymmetric catalysis. References: 3 (Russian).

**Silicon-Organic Compounds Containing Bis-Substituted symm-Triazine Cycles in Molecules**

927M0144A Tbilisi IZVESTIYA AKADEMII NAUK GRUZINSKOY SSR: SERIYA KHIMICHESKAYA in Russian Vol 17 No 3, Jul-Sep 91 (manuscript received 1 Jun 89) pp 201-206

[Article by R. A. Karamyan, M. L. Yeritsyan, N. I. Tsomaya, L. M. Khananashvili, Tbilisi State University imeni I. Dzhavakhishvili, Yerevan State Pedagogical Institute; UDC 547.872/874 + 547.1'128]

[Abstract] The title compounds were obtained starting from 1,3-di(carboethoxymethyl)-5-(2-hydroxy-3-phenoxypropyl)isocyanourate. Reaction of this compound with methylphenyldimethoxsilane at 125-135° C in presence of concentrated H<sub>2</sub>SO<sub>4</sub> gave methylphenylsiloxybis[1,3-di(carboethoxymethyl)-5-(3-phenoxyisopropyl)isocyanourate]; with methyl(phenylacetamide)diethoxysilane the product was methyl(phenylacetamido)siloxybis-1,3-di(carboethoxymethyl-5-(3-phenoxyisopropyl)isocyanourate; with  $\alpha,\omega$ -diethylaminodimethylsiloxane the product was an oligodimethylsiloxane with symm-triazine and diethylamine reactive terminal groups. References: 7 (Russian).

**Comparison of Longevity Characteristics of Solid and Highly Elastic Polymers**

927M0086A Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 320, No 1, Sep 91 (manuscript received 17 Jun 91) pp 135-139

[Article by S. B. Ratner, presented by Academician V. I. Goldanskiy 11 Jun 91, Plastics SRI, Moscow; UDC 678.74.01-19]

[Abstract] Previously published mathematical expressions describing polymer longevity in terms of time before critical breakdown, i.e. brittle rupture or loss of shape are discussed. Factors affecting longevity include fluctuations in thermal energy, load, and breakdown of intermolecular bonds. Figure 1; references 13 (Russian).

**Relationship Between Extent of Oligomeric Allyl Ester Polymerization and Its Concentration in Composition with Nonpolymerizable Substance**

927M0089B Kiev UKRAINSKIY KHMICHESKIY ZHURNAL in Russian Vol 58, Jan 92 (manuscript received 27 Dec 90) pp 103-105

[Article by S. M. Salistyy and L. M. Mironovich, Cooperative Institute, Poltava; UDC 547.42:667.633]

[Abstract] While the relationship between rate and depth of three-dimensional bulk polymerization to substrate concentration has been studied sufficiently, the same relationship for polymerization in a film has not. Introduction to the film of various non-polymerizable compounds such as plasticizers, high boiling point solvents, or other additives alters the concentration of the polymerizing substrate thereby affecting the kinetic characteristics of the polymerization process. In the present work a study was made of the relationship of polymerization rate and depth in an oligomeric allyl type film to its concentration in the composition with a non-polymerizable substance, dimethyl adipinate. The results demonstrate that introduction of the latter into the film causes an increase in the induction period of the three-dimensional polymerization. Figures 3; references 5 (Russian).

**Sorption of Chlorides of Alkaline Earth Elements by a Polymer Sorbent Impregnated With Copper Di-2-Ethylhexylphosphate**

927M0127D Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 37 No 5, May 92 (manuscript received 10 Oct 91) pp 1025-1029

[Article by A.N. Turanov; UDC 542.61:546.442]

[Abstract] The author of the study reported herein examined the distribution of alkaline earth element (calcium, strontium, and barium) chlorides between aqueous solutions and a macroporous copolymer of styrene and

divinylbenzene impregnated with copper di-2-ethylhexylphosphate. For comparison's sake, he also presented data on the liquid extraction of calcium, strontium, and barium chlorides by solutions of CuR<sub>2</sub> in chloroform. The study copolymer was synthesized by mixing weighted portions of the sorbent and CuR<sub>2</sub> in water for 5 hours. The sorption and extraction were implemented in test tubes with ground stoppers on a mixing device with a speed of 60 rpm at room temperature for 1 hour. The initial concentration of the alkaline earth elements amounted to  $1 \times 10^{-3}$  mol/l. Applying copper di-2-ethylhexylphosphate to the polymer matrix was found to significantly increase the coefficients of distribution of alkaline earth elements as compared with liquid extraction. When calcium chloride was extracted by solutions of CuR<sub>2</sub> in chloroform and heptane containing an extractive reagent of 0.1 mol/kg pure solvent, the coefficient of calcium distribution amounted to 4.05 and 8.60, respectively, versus the coefficient of calcium of distribution of 75.4 that was obtained when the copolymer of styrene and divinylbenzene impregnated with copper di-2-ethylhexylphosphate and containing 0.1 mol/kg dry sorbent was used. The coefficient of distribution of CuR<sub>2</sub> also increased when the impregnated sorbent was used; the coefficient of distribution of CuR<sub>2</sub> increased as its content in the organic or solid phases was increased. Solvating additives were found to increase the extractability of chlorides of alkaline earth elements by copper di-2-ethylhexylphosphate. Consequently, the addition of tributylphosphate to an organic phase markedly increases the coefficient of calcium distribution even though tributylphosphate alone only extracts insignificant amounts of alkaline earth elements under the same conditions. Adding tributylphosphate to the surface of an impregnated sorbent was also found to increase calcium extraction. The experiments reported herein made it possible to develop a method for preliminary sorption cleansing of calcium and strontium impurities from barium chloride. Figures 4, tables 3; references 10: 9 Russian, 1 Western.

**Investigation and Modeling of the Laws Governing Shrinkage and Mass Transfer Processes in a Polymer Base of Spherical Particles**

927M0130F St. Petersburg ZHURNAL PRIKLADNOY KHIMII in Russian Vol 64 No 12, Dec 91 (manuscript received 7 May 91) pp 2678-2683

[Article by Ya.D. Zolotonosov, G.N. Marchenko, and G.V. Ryabchuk, Volgograd Polytechnic Institute; UDC 541.127:66.661]

[Abstract] A number of contemporary processes for producing and processing high-molecular weight polymer materials involve mass transfer processes occurring in a heterogeneous multicomponent system in accordance with a sorption-desorption mechanism. Two competing processes generally affect the internal structure of the elements of the polymer material formed in such a manner. The first of these two factors is the increase in viscosity resulting from a loss of solvent, and

the second is the decrease in viscosity that occurs as the temperature rises. If a quality product to be produced, the rate at which solvent is extracted from the particles must not exceed its rate of diffusion from the polymer. In view of these facts, the authors of the study reported herein investigated and modeled the laws governing shrinkage and mass transfer processes in a polymer base of spherical particles. Specifically, they examined a synthesis process that included the removal of the low-molecular weight solvent ethyl acetate from a disperse phase and the extraction of ethyl acetate from a disperse phase, i.e., particles of polymer produced as a result of the dispersion of nitrocellulose lacquer. They plotted differential and integral curves of the distillation of solvent from spherical particles. An ISM-840 scanning electron microscope was also used to study particles' internal structure during the course of their synthesis and formation of the grain matrix. The studies performed established that in the vicinity of a 50 to 60% (mass) concentration of solvent in the gel, significant changes occur in the particles' internal structure. The nature of the microrelief in the grain underwent changes: An anisotropy with an irregular internal structure and a solid surface film 1 to 3  $\mu\text{m}$  thick was observed to form in the interval of a 2.3% (mass) concentration of ethyl acetate. This film was permeated with blind pores and isolated pores that were connected with the surrounding medium. Microphotographs also indicated the formation of a pore space between the polymer's supermolecular structures when the particles contained somewhere on the order of 0.3 to 0.5% (mass) solvent. A regular increase in the particles' apparent density and microhardness number was found to occur as solvent was removed from the particles. The vitrification point was also found to increase as the concentration of ethyl acetate in grains decreased. This finding was consistent with the general laws governing the structural transitions of known plasticized polymer systems. The authors culminated their study with the derivation of equations of the micro- and macrokinetics of the mass transfer processes that occur. When complemented with the known system of equations of external induced heating of the medium through the reactor sleeve, the said equations form a mathematical model of the process of the production and processing of high-molecular weight polymer spherical particles in accordance with the emulsion process. By using the finite differences method to solve the said differential equation system, the authors were able to determine the kinetics of the shrinkage of a polymer grain and the nature of the distribution of solvent concentration inside the particles. Figures 5, table 1; references 29: 27 Russian, 2 Western.

#### **Estimating the Effect of Modifiers on Interface Reactions in Polymer Mixtures**

927M0131E Minsk IZVESTIYA AKADEMII NAUK BELORUSSKOY SSR: SERIYA KHIMICHESKIKH NAUK in Russian No 1, Jan 92 (manuscript received 25 Mar 91) pp 105-110

[Article by S.S. Pesetskiy, Mechanics of Metal-Polymer Systems Institute, Belarus Academy of Sciences; UDC 678.046.8]

[Abstract] The author of this article has proposed a method of estimating the effect of modifiers on the interface reactions occurring in polymer mixtures. The approach recommended makes use of thermodynamic and molecular kinetics principles. The essence of the thermodynamic aspect of the proposed method lies in the fact that the compatibility in a mixture will be improved if the compatibility of the modifier with the components is greater than that of the components with one another. The theory of Flory-Huggins solutions may be used as a basis for analyzing compatibility. The thermodynamic approaches indicate (in the sense of an initial approximation) that compatibility in a given mixture will be improved when the modifier has a solubility parameter that is intermediate between the solubility parameters of the mixture's main components. The molecular kinetics aspect of the method entails an experimental estimate of the effect of the modifier on the kinetics of the formation of an adhesion contact between the components of the mixture composition. This estimate is based on a comparative analysis of the conditional rate of an increase in adhesion strength. The method entails plotting the kinetic dependence of the adhesion strength of the compounds polymer 1-polymer 2, polymer 1-modifier, and polymer 2-modifier. Besides being determined by the chemical nature of the materials, this kinetic dependence (designated  $A'$ ) is also determined by the conditions of the formation of the adhesion contact (temperature, pressure, medium, presence of impurities, etc.). A given modifier will obviously help accelerate the formation of adhesion bonds in a mixture provided that the value of  $A'$  determined for the compounds of modifiers with each of the phases is higher than the values of  $A'$  obtained for a compound of the main components with one another in the temperature interval in which the mixture was produced. The values of  $A'$  may be used as a basis for experimentally confirming the effectiveness of modifiers selected as a result of thermodynamic calculations. In this way consideration is given to the contribution that the real structure of all of the mixture's components makes to the interface reactions (i.e., the role of low-molecular weight products and those other ingredients of mixtures that are always present in real polymer materials). Specimens in the form of films are best used for determining the values of  $A'$ . Two examples illustrating the use of the proposed method of estimating the effectiveness of modifiers used in thermoplastic polymer blends are provided. Figures 3; references 11: 9 Russian, 2 Western.

#### **Inflammation Resistance of Filled Polymers Under an Impact Heat Load**

927M0133F Moscow KHIMICHESKAYA FIZIKA in Vol 11 No 2, Feb 92 (manuscript received 17 Jun 91) pp 285-288

[Article by S.Ye. Selivanov and A.A. Shiyan, Kharkov Construction Engineering Institute; UDC 536.4:691.175]

[Abstract] The authors of the study reported herein conducted a qualitative investigation of the effect that the thermophysical processes accompanying energy transformation during impact heat loads have on the occurrence of preinflammation processes in filled polymers. The primary objective of the investigation was to determine the polymer's inflammation resistance as a function of the thermophysical characteristics of both the polymer matrix and filler. The researchers began by assuming that energy with a specified intensity ( $I$ ) falls on a half-space for some period of time. Two cases were considered. In the first case, the half-space was assumed to be filled just with the matter of the matrix. In the second case, it was assumed that the filler contained material with other thermophysical properties. The qualitative analysis indicated that when a  $\text{CO}_2$  laser is used to modify epoxy polymers, it is a good idea to use a periodic pulsed mode and that reducing the surface temperature of a filled polymer during ablation processes will make it impossible for inflammation to occur. A relationship was derived for the effective inflammation activation energy (i.e.,  $\Delta E/E_e \approx 0.49$ , where  $E_e$  is the effective energy of activation of thermal oxidation of the epoxy composite,  $\Delta E = E_s - E_a$ , and  $E_a$  is the effective activation energy of thermal oxidation of the fiberglass-reinforced plastic). Estimates obtained by using the proposed relationship were in qualitative agreement (within 20%) with results obtained in actual experiments performed on a DuPont-9900 thermal analysis system with specimens consisting of an epoxy composite and a fiberglass filler in a 30:70 ratio. Figure 1; references 9 (Russian).

**Second All-Union Conference on Problems of the Physics of Polymers' Strength and Plasticity**  
**927M0133H Moscow KHIMICHESKAYA FIZIKA**  
*in Vol 11 No 2, Feb 92 pp 300-302*

[Article by G.Ye. Zaikov and D.S. Saidov]

[Abstract] The Second All-Union Conference on Problems of the Physics of Polymers' Strength and Plasticity was held in Dushanbe from 10 to 12 October 1990. It was organized by the Public Education Ministry of the Republic of Tajikistan, Tajikistan State University, and the Tajik Republic Administration of the USSR Scientific-Engineering Society. The conference was attended by 120 scientists from 20 cities throughout the Soviet Union representing 35 universities and scientific research institutes of the USSR Academy of Sciences and union republic academies of sciences, State Committee for Higher Education, higher education ministries, and various ministries and departments. Four plenary reports, 45 plenary-section reports, and 80 dais reports were presented. The conference was organized into three sections. The first was devoted to the problem of the physics of the destruction of polymers. Reports describing the process of the destruction of polymers in a highly elastic state and detailing a method of predicting the time to destruction of adhesion compounds within a broad temperature range were received with particular interest. The second section was devoted to the effect of

external factors on the structure and properties of polymers. Special attention was paid to the effect of the phase morphology of a composite based on high-density polyethylene and polyester. The third section was devoted to the structure and properties of biopolymers. Among the topics examined during the third section were the use of thermal analysis methods to determine the stability of paper containing polymer additives, the role of micro-defects in the formation of the strength and deformation characteristics of plastic composites based on nitrocellulose and active plasticizers, the use of cellulose ethers to reinforce filled composites, and the use of various analysis techniques (including EPR and IR spectroscopy) to study the destruction of biopolymers. Fifteen plenary-section reports were delivered in the first section along with 30 dais reports. Thirteen plenary-section reports and 25 dais reports were delivered during the second section, and 17 plenary-section and 25 dais reports were delivered in the third section. The third all-union conference on polymers' strength and plasticity is to be held in 1995. Materials for the planned conference are being collected by the libraries of Tajik State University in Dushanbe and the Chemical Physics Institute imeni N.N. Semenov in Moscow.

**Investigation of Electroconducting Polymer Composition Structures by Spin Probe Method**

**927M0144B Tbilisi IZVESTIYA AKADEMII NAUK GRUZINSKOY SSR: SERIYA KHIMICHESKAYA**  
*in Russian Vol 17 No 3, Jul-Sep 91 (manuscript received 20 Jun 89) pp 224-228*

[Article by Dzh. N. Aneli, D. G. Pagava, Georgian Scientific Research Institute of Energetics and Hydro-technical Constructions; UDC 541.64.539.199:543]

[Abstract] The interest in electroconducting polymers has increased significantly in recent past. The electroconducting properties depend on the distribution of the conducting component in the polymer matrix. The EPR spectroscopic method of the spin probe was used to investigate structural characteristics of the conducting compositions and to determine the effect of the concentration of conducting components on the microstructure of such materials. The radical probe inserted into the composition matrix and localized in the micropores yields information on local density of the material and thus evaluate the homogeneity of the distribution of filler particles. The nitroxide radical (such as 2,2',6,6-tetramethylpiperidine-1-oxyl) was used as the radical probe. The study material was prepared from silicon-organic rubber filled with soot and hardened with diethylaminomethyltriethoxysilane. It was established that the distribution of the soot was a determining factor in evaluating the homogeneity of the sample conductivity. An assumption was made that at high concentrations of the soot the probability of the filling of intermolecular spaces and micropores was higher than in compositions with lower concentration of the soot. Thus it was shown that the spin probe method made it possible to describe the microstructure of a filled electroconducting resin and

to some extent to evaluate the homogeneity of the distribution of the filler particles in the elastomer matrix. Figures 3; references: 5 (Russian).

### Mechanism of Particle Structure Formation in Latexes From Microcomposition Polymers

927M0147A Moscow KOLLOIDNYY ZHURNAL in Russian Vol 54 No 1, Jan-Feb 92 (manuscript received 15 Apr 91) pp 42-46

[Article by V. I. Yesileyeva, S. V. Bogdanova, Institute of Physical Chemistry, USSR Academy of Sciences, Moscow; UDC 541.18.05 + 541.64 + 542.952]

[Abstract] Studying the mechanism of the formation of latex particles morphology in aqueous phase, the attention is paid to the changes in the network of the hydrogen bonds in the structure of the border layers in water during the appearance of highly dispersed polymer phase. In previous work the polarity of the polymer phase was evaluated by interphase tension of the corresponding monomer at the contact with water without consideration of possible effect of the emulsifier contained in the latex. In the present work the effect of this factor was considered during investigation of the structure of particles formed during consecutive polymerization of two monomers with different polarity and, correspondingly, the interphase tension on the border between water-methacrylate and 1,1'-dihydroperfluoroheptylacrylate. The significance of this change in interphase interactions between the monomer and water under the influence of the adsorption of the emulsifier used in the synthesis of latex was demonstrated. Tables 2; Figures 3; references 8: 5 Russian, 3 Western.

### Evaluation of Parameters of Adsorption-Solvate Layers, Formed on Filler Surfaces in Polymer Solutions

927M0148E Moscow KOLLOIDNYY ZHURNAL in Russian Vol 54, No 2, Mar-Apr 92 (manuscript received 4 Sep 90) pp 154- 157

[Article by S. N. Stepin, F. R. Bogatov, and N. V. Svetlakov, Chemical Technological Institute, Kazan; UDC 541.18.051:678.7]

[Abstract] Aggregate stability is one of the most important technological characteristics of suspensions of inorganic fillers in polymer solutions, such as paints and lacquers used in making magnetic tape. The tendency of such thermodynamically unstable systems to coagulate is chiefly determined by the thickness and composition of the adsorption-solvate layers formed on the particle surfaces of the dispersed phase. The most common method used to study processes taking place at the interface during preparation of suspensions of filler in polymer solutions consists of studying the adsorption of polymers on the solid phase surface. However, the results are often presented in the form of Gibb's adsorption as a function of the concentration of the equilibrium solution of the polymer (adsorption isotherm), which does not lend itself to single value treatment, and evaluation of the adsorption-solvate layer parameters is not possible. In the present work a method is presented for calculating the parameters of the adsorption-solvate layers formed on the surfaces of filler particles in polymer solutions that is based on the combined use of the results of adsorption studies and an evaluation of the rheological properties of the suspensions formed. Calculated results were experimentally verified with an independent determination of the adsorbed layer parameters on the surfaces of ferric gamm-oxide particles suspended in an ethyl acetate solution of partially saponified vinyl chloride-vinyl acetate copolymer. Figures 2; references 5: 3 Russian, 2 Western.

**The Ion-Exchange Behavior of Kurchatovium in Hydrofluoric Acid Solutions**

927M0121A Leningrad RADIOKHIMIYA in Russian  
Vol 33 No 6, Nov-Dec 91 (manuscript received  
19 Apr 91) pp 90-99

[Article by Z. Shelgovski, V.P. Domanov, V. Glazberg, I. Zvara, and Yu. Ts. Oganesyan, Nuclear Research Institute, Dubna; Kh. Brukhertzayfer, Isotope and Radiation Research Institute, Leipzig, FRG; L.I. Guseva and G.S. Tikhomarova, Geochemistry and Analytic Chemistry Institute imeni V.I. Vernadskiy, Moscow; and M. Yussenuya, Nuclear Physics Institute, Orse [transliteration]; UDC 546.799.94]

[Abstract] A quick method has been developed for continuous separation of a kurchatovium fraction while reliably purifying it of the heavy actinoids formed when  $^{248}\text{Cm}$  is irradiated with  $^{18}\text{O}$  ions. The new method also provides for identification of  $^{261}\text{Ku}$  ( $T_{1/2} = 65$  seconds) based on the long-lived decay products  $^{233}\text{Fm}$  ( $T_{1/2} = 3$  days) and  $^{253}\text{Es}$  ( $T_{1/2} = 20$  days). Standard commercial radioisotopes ( $^{95}\text{Zr}$ ,  $^{181}\text{Hf}$ ,  $^{249}\text{Cf}$ ,  $^{152-155}\text{Eu}$ ,  $^{88}\text{Y}$ ,  $^{139}\text{Ce}$ ,  $^{160}\text{Tb}$ ,  $^{170}\text{Tm}$ , and  $^{173}\text{Lu}$ ) and commercial ion-exchange resins (Dowex 50x80 [20 to 70  $\mu\text{m}$ ] cation exchanger, Aminex [12-16  $\mu\text{m}$ ] cation exchanger, and Dowex 1x8

(30 to 70  $\mu\text{m}$ ) anion exchanger) were used during the course of the development of the new extraction method. According to the new procedure, an aerosol stream (KCl) is used to transfer nuclear reaction products from an irradiated target to chemical separating equipment. The aerosol particles and the radionuclides that they have adsorbed are dissolved in 0.2 mol/l hydrofluoric acid. Next, the said solution is passed through three ion-exchange columns (Teflon tubes filled with resin and sealed with porous Teflon plugs at both ends). The transplutonium elements formed during nuclear reactions are extracted from the solution in the first column, which is actually a cation-exchange column. Kurchatovium is trapped in the second (anion-exchange) column, and the kurchatovium decay products are concentrated in the third column (a second cation-exchange column). During the course of the studies reported herein, researchers were able to demonstrate for the first time that in hydrofluoric acid solutions, kurchatovium forms stable anionic complexes that may be adsorbed by an anion exchanger. In other words, they were able to demonstrate that kurchatovium behaves analogously to Zr and Hf, i.e., to group IV transition elements in the Periodic Table of Elements. Figures 3, table 1; references 16: 6 Russian, 10 Western.

**Formation Mechanism of Vaulted High Contrast Aureoles of Diamond Mineral-Satellites on Local Paleo Plateaus**

927M0086C Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 320, No 2, Sep 91 (manuscript received 19 Jun 91) pp 169-173

[Article by O. G. Saltykov and Yu. M. Erincheck, presented by Academician N. A. Shilo 20 May 91, Geology SRI (A-U), Leningrad; UDC 553.068.5: 552.323.6(571.56)]

[Abstract] A series of polygenic, mineralogical aureoles of late paleozoic age was discovered on the east rim of the Tunguss synclise in the Yakutsk diamond-bearing province. The aureoles consist of sparse geological bodies containing kimberlite minerals (pyrope, picroilmenite, chromospinelide, and diamond) with traces disseminated throughout elevated formations of upper paleozoic strata where high contrast aureoles of diamond mineral-satellites stand out sharply. The local paleo plateaus are square kilometers in size and 30-50 meters high. Normally, such aureoles contain sufficiently large sized grains (0.5-4 mm) of kimberlite minerals. In the present work a possible mechanism for the formation of these aureoles is presented. It is further noted that these aureoles are concentrators of heavy minerals and thereby present considerable interest as possible alluvial deposits. Figure 1; references 4 (Russian).

**Isotope-Oxygen Features of Ilmenite from Diamond-Bearing Kimberlite Pipes**

927M0086D Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 320, No 1, Sep 91 (manuscript received 19 Jun 91) pp 174-176

[Article by Yu. A. Borshchevskiy and T. N. Laverova, presented by Academician V. A. Zharikov, Lithosphere Institute, Moscow; Moscow State University imeni M. V. Lomonosov; UDC 550.423]

[Abstract] Oxygen isotope study of ilmenite, one of the most widely distributed satellite minerals of diamond in kimberlite pipes, may yield valuable information on the genesis and transformations of kimberlite pipes as well as on the mechanism of natural diamond formation. In the present work a study was made for the first time on the oxygen isotope composition of mono-mineral ilmenite nodules from several pipes in the Arkhangelsk and Yakutsk kimberlite provinces. Total oxygen separation was achieved by means of a previously published technique and isotope composition determined by mass spectrometer using NBS-28 standard. A marked difference in the  $O^{18}$  content of ilmenites from the above provinces reflecting genetic uniqueness and geological-geochemical specifics of kimberlite pipes of each province was established, thus making it possible to assume that the oxygen isotope characteristics of ilmenite may be used to evaluate potential diamond-bearing capabilities of kimberlite pipes. The oxygen isotope features of ilmenite also yields information on the genesis and

geological-geochemical evolution of kimberlite pipes, as well as in estimating potential diamond-bearing capability. Figure 1; references 12 (Russian).

**Technogenic Amalgamation of Placer Gold: Physical and Chemical Consequences**

927M0086E Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 320, No 1, Sep 91 (manuscript received 27 May 91) pp 197-198

[Article by V. L. Shevkalenko, L. N. Shokina, and V. V. Kryachko, presented by Academician N. A. Shilo 20 May 91, Mining Institute, Khabarovsk; UDC 553.411.04]

[Abstract] Placer deposits in the Far East have been exploited since 1852 and until recently, mercury was used to collect gold from the tailings, thereby making it a common occurrence in technogenic products under the climatic conditions of the Far East. A physical consequence of the presence of mercury is the aggregation of fine gold grains in solid adhesions with or without connate coatings of mercury. A study was made of a single mercury drop obtained in 1977 while washing technogenic tailings of a previously worked placer deposit. Detailed study of the remaining gold demonstrated that during the course of time and temperature changes, some of the gold leached out of the nodule and was either dissolved in organic acids present in the river water, or simply washed away. Figure 1; references 2 (Russian).

**Composition of Pt-Fe-Solid Solutions as Indicator of Depth of Erosion Shearing of Platinum-Bearing Alkali-Ultrabasic Ring Intrusions**

927M0087A Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 321, No 5, Dec 91 (manuscript received 11 Oct 91) pp 1049-1053

[Article by Corresponding Member Academy of Sciences I. Ya. Nekrasov, V. V. Ivanov, A. M. Lennikov, R. A. Oktyabrskiy, B. L. Zalishchak, V. I. Sapin, and V. I. Taskayev, Geology Institute (Far Eastern), Vladivostok; UDC 553.491.8:553.262.2]

[Abstract] The determination of the magnitude of erosion shearing and estimating the vertical spread of mineralization in potential metal-bearing magmatic massifs is urgent from both a practical standpoint as well as for typifying and revealing bedrock sources of alluvial deposits. It may be resolved on the basis of geological and structural reconstruction of ores and detailed study of mineral compositions and associations deposited along hypsometrically different levels of ore-bearing intrusions. Gold testing is one of the orienting mineral-geochemical criterion for estimating the magnitude of erosion shearing in gold deposits. Regarding platinoids, the composition of Pt-Fe alloys, widely distributed in both alluvial and bedrock sources, may serve as such an indicator. In the present work this concept was tested by

evaluating the composition of Pt-Fe solid solutions in respect to the extent of crystallization in annular alkaline-ultrabasic massifs for the first time. This concept may be further improved as more data are accumulated. Figure 1; references 10 (Russian).

#### Factors of Regenerative Genesis of Gold-Quartz Mineralization in Chukotki

927M0088A Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 320, No 6, Oct 91 (manuscript received 12 Aug 91) pp 1433-1437)

[Article by A. V. Volkov, presented by Academician N. A. Shilo, Northwest Department Nonferrous and Rare Metal Geological Prospecting Central SRI, Magadan; UDC 553.411.551(571.41)]

[Abstract] There are two gold ore regions within the confines of Central Chukotka that differ from each other. The first region contains gold-silver, gold-quartz, gold-rare metal, gold-antimony, and gold-sulfide disseminated volcanic-plutonic mineralization, while the second contains metamorphogenic-plutonogenic gold-quartz mineralizations localized in folding paleozoic structures. In the first region close mineral-geochemical relationships were detected between veined and disseminated mineralizations. In the present work some factors of regenerative genesis of gold-quartz mineralizations are listed giving both regional and local factors. It appears highly probable that these gold-quartz mineralizations were formed as a result of regeneration of mineral matter from both intruding rock as well as from earlier gold-sulfide disseminations. Thus two types of deposits are possible. The first type is formed as a result of epeirogenic regeneration, normally containing insignificant gold reserves, and a second type, formed as a result of multi-stage regeneration and being more promising. The results of the study will aid in predicting both the locations of new deposits and their scale. References 8: 7 Russian, 1 Western.

#### Isotope Composition of Pb and Pb-Pb-Age of Siberian Kimberlites

927M0088B Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 320, No 6, Oct 91 (manuscript received 9 Aug 91) pp 1466-1469

[Article by N. N. Fefelov, S. I. Kostrovitskiy and N. V. Zarudneva, presented by Academician V. L. Barsukov 9 Aug 91, Earth's Crust Institute, Irkutsk; Geochemistry Institute imeni A. P. Vinogradov, Irkutsk; UDC 550.44:550.93]

[Abstract] The origins of plutonic ores such as kimberlite are being successfully resolved by comprehensive research including Pb, Nd, and Sr isotopes. Of these elements, only the isotope composition of Sr has been studied in the USSR. The present work provides the first data on the isotope composition of Pb in kimberlites of Yakutiya and Prisayanya. Pb 206/204, 207/204 and

208/204 ratios are listed for 24 samples from various Siberian pipes. The conducted approbations demonstrate the possibility of Pb-Pb dating in bulk tests of kimberlites. References 10: 7 Russian, 3 Western.

#### X-Ray Diffraction Study of Chlorochalcogenide Complexes of Platinum

927M0089A Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 58, Jan 92 (manuscript received 7 Dec 90, after revision 8 Apr 91) pp 12-16

[Article by V. B. Rybakov, L. A. Aslanov, S. V. Volkov, V. I. Pekhno, N. I. Timoshchenko (Deceased), and Z. A. Fokina, Moscow State University; General and Inorganic Chemistry Institute, Kiev; UDC 539.26: 546.13.22.23.24.95]

[Abstract] Chalcogen chlorides are aprotic solvents and also serve as effective low temperature chlorinating agents. For this reason they are frequently used to regenerate platinum-containing stocks. In the present work a study was made of the crystal structures of chlorochalcogenide complexes of platinum to enable further study of the structure of reaction products formed during the regeneration process. X-ray diffraction was used to analyze the crystal structure of platinum complexes having the general formula  $\text{PtE}_2\text{Cl}_8$ , where E is S, Se, or  $\text{PtTe}_2\text{Cl}_{12}$ . It was demonstrated that in the first two isostructural complexes, the platinum atom is surrounded by four chlorine atoms and two chalcogen atoms in a distorted octahedron. In the tellurium-containing complex, the platinum atom is surrounded in a parallel octahedron with only chlorine atoms. Figures 2.

#### Electrophoretic Behavior of Aggregates of Ultradisperse Diamond Particles

927M0114A Moscow KOLLOIDNYY ZHURNAL in Russian Vol 53 No 6, Nov-Dec 91 pp 1067-1071

[Article by A.G. Ovcharenko, A.B. Solokhina, R.R. Satayev, and A.V. Ignatchenko, Altay Scientific Production Association, Biysk; UDC 537.363:541.182.6]

[Abstract] A new type of diamond, i.e., ultradisperse diamond, that is produced directly from explosives has come to enjoy wide-scale use in the creation of composite electrophoretic coatings. Aqueous dispersions of ultradisperse diamonds have been produced commercially for some time now, and electromembrane methods of removing their ionic impurities have been developed. The change in the surface properties of diamond when particle size is reduced to the cluster state is thus interesting from a theoretical standpoint. In view of these facts, the authors of the study reported herein examined hydrosols of ultradisperse diamonds. Specifically, they used the macroelectrophoresis method to study the dependence of electrophoretic mobility on temperature and potassium chloride concentration.

During the course of their studies, the researchers considered temperatures within the range from 30 to 60°C, potassium chloride concentrations of  $10^{-2}$  to  $10^{-4}$  M, and pH levels from 3 to 10. Commercial ultradisperse diamonds conforming to specification TU 84-1124-87 were used for the studies. Membrane methods (electrofiltration and electrodialysis) were used to purify the dispersions and to bring the study solution to a pH of 6.8 with an acid content not exceeding  $10^{-6}$  mol/l. Potassium chloride, hydrochloric acid, and potassium hydroxide were used to create the required pH and ionic strength in the working solutions. The ratio of solid phase and solution amounted to 1:30,000. The electrophoretic mobility of the study solutions was measured in a thermostatted U-shaped tube after 1 to 3 days of preparation of the solutions. On the basis of the change in optical density in potassium chloride solutions they determined regions of rapid and slow coagulation ( $10^{-2}$  in the case of rapid coagulation and  $5 \times 10^{-4}$  to  $10^{-3}$  M in the case of slow coagulation). The model of aggregation of ultradisperse diamond adopted by the authors assumes the presence of both primary and secondary structures. In accordance with this model, they were able to calculate the  $\zeta$ -potential electrophoretic mobility data in accordance with the known formula that is valid for particles with unipolar conduction (ion exchangers). The  $\zeta$ -potential values thus calculated were close to those for natural diamond consisting of nonaggregated particles with a radius of 0.25  $\mu\text{m}$ . When the ionic strength was kept constant at 0.01 M, the negative value of the  $\zeta$ -potential was found to increase as the solution's pH increased. In this respect, the ultradisperse diamond was essentially no different from other synthetic or natural diamonds. The electrophoretic behavior of hydrosols of ultradisperse diamond was found to be unusual, however. The increase in electrokinetic potential with temperature that was observed in the case of solutions with an ionic strength of  $5 \times 10^{-4}$  M is generally linked to the destruction of the water's boundary layer. The slope of the curve plotted for solutions of the said ionic strength was found to be analogous to that of quartz, thus pointing to the possibility of the existence of a water boundary layer at the diamond's surface. As the ionic strength was increased (from  $5 \times 10^{-4}$  to  $10^{-2}$  M), however, the situation became reversed: Increasing the temperature caused a decrease in the  $\zeta$ -potential. This unusual behavior of ultradisperse diamond was attributed to a change in the structure of the aggregates (for example, to the formation of a secondary structure and its packing). The authors concluded that the most likely cause of this phenomenon is the destruction of the boundary layers and acceleration of the coagulation process as the temperature increases. The authors concluded by stating that the presence of a significant temperature-dependent structural factor must be taken into account when stabilizing hydrosols of ultradisperse diamond. Figures 3; references 11 (Russian).

### The Crystal Chemistry of Layered Metal Oxohalides and Oxochalcogenides (Sillen Phases)

927M0127A Moscow ZHURNAL  
NEORGANICHESKOY KHIMII in Russian Vol 37  
No 5, May 92 (manuscript received 21 Jun 91)  
pp 970-984

[Article by V.A. Dolgikh and L.N. Kholodkovskaya, Moscow State University imeni M.V. Lomonosov; UDC 546.87.21.121]

[Abstract] The authors of this review have systematized the crystal chemistry information developed regarding layered metal oxohalides and oxochalcogenides that has been accumulated since Sillen and his coworkers synthesized and investigated the first complex bismuth oxohalides more than 50 years ago. The said compounds are made up of alternating plane layers of  $M_2O_2$  (or  $M_3O_4$ ) and one, two, or three layers of halogen (chalcogen). The authors have based their systematization of the said compounds on a new convention. Specifically, in addition to the letter "X" that is used in the crystal chemistry formula of Sillen compounds to designate a monatomic layer (or layers) of some element and the subscript numeral used to designate the "thickness" of the halogen layers, they use a superscript numeral to designate the "thickness" or number of metal "sublayers" in the metal-oxygen fragment. The reviewers focus their attention on Sillen phases and the similarity and differences between them and the more recently discovered Aurivillius phases, which are very closely related to Sillen phases from a crystal chemistry standpoint. The main difference between the two families of compounds is shown to be the fact that Aurivillius compounds represent  $Bi_2O_2$  layers separated by perovskite-like layers, whereas Sillen phases are based on plane fluorite-like layers. The reviewers conclude by mentioning the recent synthesis of several phases that besides possessing the perovskite and NaCl types of blocks that are characteristic of high-temperature superconductors, also include fluorite-like  $M_2O_2$  layers and that thus represent a "bridge" family between Sillen and Aurivillius compounds. Figures 7, tables 6; references 61: 15 Russian, 46 Western.

### Complex Formation of Transition Metal Ions in Aqueous Suspensions of Graphite Oxide

927M0127E Moscow ZHURNAL  
NEORGANICHESKOY KHIMII in Russian Vol 37  
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[Article by N.I. Kovtyukhova, G.A. Karpenko, and A.A. Chuyko, Surface Chemistry Institute, Ukraine Academy of Sciences, Kiev; UDC 546/261+562/541.49]

[Abstract] The authors of the study reported herein examined the complex formation of ions of copper (II), nickel (II), cobalt (II, III), and chromium (III) in aqueous suspensions of graphite oxide. The study metal ions were sorbed at room temperature from aqueous or water-and-ammonia solutions of their salts:  $CuSO_4$ ,  $NiCl_2$ ,

$\text{Co}(\text{NO}_3)_2$ , and  $\text{CrCl}_3$ . Graphite oxide was produced by the oxidation of graphite bisulfate with potassium permanganate in concentrated sulfuric acid. It was rinsed with water until a pH of 5.7 was obtained. The finished product was a brown suspension containing 1.8% dry matter. The starting solutions of  $\text{Cu}^{II}$ ,  $\text{Ni}^{II}$ , and  $\text{Cr}^{III}$  ammoniates were prepared by mixing solutions of the respective salts with a 25% solution of  $\text{NH}_3$  in the quantity required so that the pH of the reaction mixture would be between 8 and 12. The reaction mixture was stirred for 1.5 hours until equilibrium was reached and was then filtered off. The concentration of metal ions in the filtrate was determined by trilonometric or iodometric titration in accordance with the standard methods. In the absence of ammonia (i.e., in aqueous solutions), less than 2% of the  $\text{Co}^{II}$  ions (by weight) were absorbed, and the  $\text{Cu}^{II}$ ,  $\text{Ni}^{II}$ , and  $\text{Cr}^{III}$  ions were, for all practical purposes, not absorbed at all. Sorption of the metal ions increased significantly when ammonia was present in the solution. The studies performed confirmed that the amount of metal complexes formed in the carrier phase depends on the pH of the medium. The maximum amount of bound ions was observed at pH levels of 10 to 11. The electron and infrared spectra of the compounds synthesized indicated that the metal ions are implanted into the layer structure of the graphite oxide in the form of aqua amino complexes and coordinated through the oxide's structural hydroxyl and carbonyl groups. Figure 1, tables 3; references 9: 2 Russian, 7 Western.

**Chemical Coating of Ceramic With a Silver Film**  
927M0130G St. Petersburg ZHURNAL PRIKLADNOY KHIMII in Russian Vol 64 No 12, Dec 91 (manuscript received 20 Jun 91) pp 2693-2695

[Article by Yu.S. Kononov, G.N. Parshikova, L.I. Korneva, V.P. Plekhanov, and O.L. Reshetnikov, Chemistry and Chemical Metallurgy Processes Institute, Siberian Department, Russian Academy of Sciences; UDC 661.9:666.3.037.5:686.43]

[Abstract] The purpose of applying silver to ceramic is to produce an anisotropic gas-separating membrane. Silver performs a separating function in the membrane because of its selective transmission for oxygen, and the ceramic serves as the basic membrane. Such membranes must be continuous; at the same time, their silver coatings must be as thin as possible to permit the maximum gas flow. The authors of this communication have described a process for coating 8-mm-diameter ceramic tubes with silver and then using the tubes to manufacture gas-separating elements. Before being coated, the ceramic is degreased in alcohol and chromic acid and etched with a mixture of hydrofluoric and hydrochloric acids (this does not apply to tubes based on silicon and aluminum oxides). The ceramic tubes are sensitized in a stannous chloride solution and then rinsed two to three times by immersion in distilled water for 30 minutes. Carbon-based tubes withstand all of these preparatory operations and are thus preferred. The distinction of the chemical

silver plating technique recommended by the authors is the use of a 10% solution of nitric acid silver without a reducing agent in order to avoid reducing the silver in bulk and the formation of a metal precipitate with a poor bond to the ceramic surface. By using the stannous chloride adsorbed by the ceramic to reduce the silver, the authors were able to deposit the silver just on the ceramic. When the ceramic is rinsed well after the sensitization operation, metallic silver does not form in the solution, and the ceramic builds up a silver coating gradually. The operation is completed after 1 to 2 days, at which time the tubes are rinsed in water and dried at 100°. An electron microscope (resolution, 1  $\mu\text{m}$ ) was used to inspect the quality of tubes coated by using the new technique. No breaks in the silver coatings were detected, although the thickness of the coatings produced did prove to be quite irregular at some spots. At most sites along the tubes inspected, the thickness of the silver coating did not exceed 1,000 angstroms. Figures 2; references 2 (Russian).

#### Quantum Chemistry in Moldova

927M0135A Moscow KHIMICHESKAYA FIZIKA in Vol 11 No 5, May 92 pp 588-594

[Article by I.B. Bersuker; UDC 541.71]

[Abstract] Nikolay Dmitrievich Sokolov was a key individual in the development of quantum chemistry in the USSR in the postwar period. He was one of the organizers of the First All-Union Conference on Quantum Chemistry in Leningrad in 1961 and later directed the organization of the second and third all-union conferences as well. Thanks to his opposition, a 1964 decision to transfer a group of quantum chemists working at the Chemistry Institute in Kishinev (since 1959) to the mathematics department was reversed. Also of great significance to the advancement of quantum chemistry in the USSR were Sokolov's reviews of the subject, his evaluations, comments, and support of different directions in research on the structure of molecules. Moldova has also been the site of a great deal of research in various areas of quantum chemistry. The first big Moldovan contribution in the area of tunnel (inversion) cleavages was the prediction of tunnel cleavages of vibron states and the effects resulting from this cleavage. The vibron origin of the configurational instability of molecular systems and multimode and multiple-center Jahn-Teller effects are other areas in which scientists in Moldova have made important progress. Quantum chemists in Moldova have also done important work in relation to mixed-valence compounds: Besides discovering distinctive features in the electron spectra and magnetic properties of mixed-valence compounds, Moldovan scientists predicted and confirmed "partial delocalization" effects in them and have developed the new principle of micromolecular electronics-based devices (e.g., molecular switches, transistors, and memory cells based on the possibility of controlling electron transfer by changing the properties of bridge atom groups between centers by means of external

effects. The orbital vibron problem and chemical activation in catalysis represent other areas in which Moldovan scientists have been active: The theory of vibron activation has been successfully applied to the analysis of the activation of small molecules in coordination compounds and on their surfaces. Quantum chemists in Moldova have also done extensive work on biological problems, including a series of studies involving electron transfer in mixed-valence compounds wherein electron transfer in ferredoxin has been studied. Moldovan quantum chemists have applied the vibron theory of ferroelectricity to crystals and crystal chemistry. A pseudo-Jahn-Teller effect has been postulated as an explanation for the occurrence of spontaneous lattice polarization and ferroelectricity in BaTiO-type perovskites and has served as the basis for a series of research projects on the vibron theory of ferroelectricity. These same ideas have been used to explain the liquid-crystal and gas-liquid transitions. Moldovans have also done extensive research on a cooperative Jahn-Teller effect in orthovanadates and other crystals. Among its other concrete results, this line of research has led to the prediction of gigantic magnetostriction of a series of Jahn-Teller crystals, the possibility of controlling phase transitions by means of a magnetic field, and new types of structural phase transitions in mixed crystals in particular. There are three other areas of quantum chemistry in which scientists in Moldova have been especially active. The first is the theory of physics research methods (including EPR and Mossbauer spectra, infrared spectra, the shape of optical absorption and luminescence bands, birefringence, polarizability, and hyperpolarizability). The second area is that of a method of calculating electron structure (notably a quasi-relativistic LCAO-MO [linear combination of atomic orbitals in a molecular orbital] method and a method of fragment-by-fragment calculation). The third area is that of methods of predicting the biological activity of molecular systems. This includes a method that is based on describing molecules in terms of their electron structure in conjunction with conformation (geometry, topology) reduced to one electron topology matrix and on compiling electron topology matrices of a series of compounds along with their biological activity (inactivity). This method has been used to predict the biological activity of a number of enzyme activity inhibitors, plant growth and development regulators, and defoliants. References 28: 14 Russian, 14 Western.

#### A Study of the Mechanism of Internal Rotation in Solids Based on Data on the Intermolecular Contribution to Spin-Lattice Relaxation. Benzene Crystals

927M0135B Moscow KHIMICHESKAYA FIZIKA  
in Vol 11 No 5, May 92 pp 724-733

[Article by N.K. Gaysin and T.N. Khazanovich, Kazan Chemical Technology Institute and Chemical Physics Institute imeni N.N. Semenov, Russian Academy of Sciences, Moscow; UDC 541:143]

**[Abstract]** The authors of the study reported herein examined the intermolecular contribution to spin-lattice relaxation in benzene molecules. Specifically, they focused their attention on just how sensitive this intermolecular contribution is to the mechanism of reorientation of the molecules in the plane of their rings. The studies were based on a model according to the molecules are subjected to "weak disturbances" resulting in transfers to the nearest equilibrium position as well as "strong disturbances." Because of the latter, the molecule may end up in any equilibrium position. The innovation of the present study is that both "strong" and "weak" disturbances are taken into consideration in an effort to determine which mechanism predominates in the benzene crystals studied. The interrelationship of the given molecules with their neighboring molecules was taken into consideration when the intermolecular contribution was analyzed. Specifically, three very simple cases were examined. According to the first model, the two molecules were assumed to be rotating independently of one another. In the second model it was assumed that molecules are always rotating at angles that are identical in size but opposite in direction. In the third scenario considered (termed the Anderson or "ultrastrong" disturbance model) it was assumed that because of a strong disturbance, both molecules had an equal probability of ending up in any one of 36 equilibrium positions accessible to them. The intramolecular contribution to spin-lattice relaxation in the specific case of benzene was also taken into consideration. The analysis performed established that the intermolecular contribution is strongly dependent on the parameter characterizing the relative intensity of the "strong" and "weak" disturbances. The analysis revealed that the Anderson model (i.e., the model of "ultrastrong" disturbances) should be rejected because it results in significant deviations from experimentally obtained values. The authors were unable to select between the first and second models on the basis of the experimental data available to them. They speculated that it will be possible to choose between the two models in the future as measurements become more precise and as the resonance frequency range is expanded. Figure 1, table 1; references 20: 6 Russian, 14 Western.

#### Use of Mathematical Methods and Computers in Intensive Agriculture

927M0143b Moscow KHIMIZATSIYA SELSKOGO KHOZYAYSTVA No 10, Oct 91 pp 49-58

[Article by L. V. Arutyunova, All-Union Scientific Research Institute of Fertilizers and Agronomic Soil Science; UDC 681.142.37:631.151.2]

**[Abstract]** The All-Union Scientific Research Institute of Fertilizers and Agronomic Soil Science has developed an automated information and calculation system for the collection, analysis, and correlation of agricultural field data and for the development of recommendations in the use of agricultural chemicals. One of the most important tasks of this system is the construction and use of

multifactorial regression equation models. Models in use include soil science, agricultural meteorology, and phytopathology. Expert systems and models based on empirical data are also employed. Data bases containing information about physical, chemical, and biological properties of the soil in the various zones of Russia, as well as weather and climate, and the use of pesticides and fertilizers, have been formulated. The data bases include experimental results and historical data. However, ecological data, which is necessary for successful application of many models, is lacking. A system of agroecological monitoring is being developed to correct this situation. Work is proceeding on a prognosticative ecological model system, to be used for evaluating the possible contamination of plants, soil, and surface and subsurface water as a result of using chemical agents. Figures 3; references 8: 7 Russian, 1 Western.

### Innumerable Diamonds

93P60012A Tashkent *PRAVDA VOSTOKA* in Russian  
27 Aug 92 p 1

[Text]

### Diamond Sales

The celebrated storehouse of Russian precious stones—the Diamond Fund—was recently enriched with yet

another unique exhibit—a Yakutsk diamond weighing 241.7 carats that has been named "Free Russia." This find was a remarkable event in the almost 40-year diamond era of Yakutiya.

On the 360th Anniversary of Yakutiya becoming part of Russia, a federal agreement has been signed, according to which the riches of its interior, water, and forests have become the property of the people of the Republic of Sakha (Yakutiya). Local natural resources can now be used only with the permission of the government of the republic, and of course, for considerable payment.

How does the republic now intend to dispose of its riches? With regard to diamonds, Yakutiya will sell the main part to the South African Company De Beers, which controls 80 percent of these precious stones on the worldwide market. According to the President of the Republic M. Nikolayev, this method of diamond sales for Yakutiya is the most rational. To enter the world market independently today would lower the price for the goods, and millions would be lost.

But the republic is not limited to sales only of raw diamonds, but will process them itself. A special company has been created, which will begin to manufacture cut diamonds.

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5 Nov 1992